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Wood-derived compounds known to possess toxicity toward fish and to be present in pulp mill effluents include resin and unsaturated fatty acids, their chlorinated analogs, chlorinated guaiacols, and epoxystearic acid. The objective of this investigation has been to assess the extent to which these compounds are removed from pulp mill effluents by different waste treatment systems in use in several locations in the United States. Effluents before and after treatment were collected and submitted for determination of the compounds of interest. Nearly all of the waste treatment processes studied removed the toxic compounds effectively. Although primary clarification had little effect on these materials, aerated lagoons and air-activated sludge systems normally removed from 80 to 100% of the resin and fatty acids and their chlorinated analogs from kraft and sulfite mill effluents. Biological treatment facilities which exhibited poorer fatty and resin acid removal were those which received high loadings of fatty and resin acids and BOD. High loadings were apparently reflected also in the lower percentage removal of the toxic compounds in the two oxygen-activated sludge systems studied. Large reductions in concentrations of the toxicants were observed following precipitation processes. Systems studied included lime precipitation and tertiary treatments employing alum. Reverse osmosis demonstrated essentially complete rejection of fatty and resin acids. Performance of pilot ultrafiltration units was either good or marginal, apparently depending upon the type of membrane used. Although chloroform contents of the samples were affected minimally by ultrafiltration, they underwent reduction of from 85 to 97% in all of the other treatment systems studied.

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REMOVAL OF WOOD-DERIVED TOXICS FROM PULPING AND BLEACHING WASTES

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory – Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report "Removal of Wood-Derived Toxics from Pulping and Bleaching Wastes" is intended to identify and quantify the presence of certain organic compounds which appear to exert a toxic impact in the water environment. These compounds derive from the extractable portion of wood substance and consist of some of the resin acids and unsaturated fatty acids as well as chlorinated organics from pulp bleaching. Through the cooperation of fifteen mills in the United States samples were obtained for analyses. This report contains the results of the analytical work. The findings indicate that some treatment processes and in-plant measures are capable of destruction or control of these organics. No attempt is made to relate the presence and quantity of these organics to their effect on receiving waters.

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ABSTRACT

Wood-derived compounds known to possess toxicity toward fish and to be present in pulp mill effluents include resin and unsaturated fatty acids, their chlorinated analogs, chlorinated guaiacols, and epoxystearic acid. The objective of this investigation has been to assess the extent to which these compounds are removed from pulp mill effluents by different waste treatment systems in use in several locations in the United States. Effluents before and after treatment were collected and submitted for determination of the compounds of interest.

Nearly all of the waste treatment processes studied removed the toxic compounds effectively. Although primary clarification had little effect on these materials, aerated lagoons and air-activated sludge systems normally removed from 80 to 100% of the resin and fatty acids and their chlorinated analogs from kraft and sulfite mill effluents. Biological treatment facilities which exhibited poorer fatty and resin acid removal were those which received high loadings of fatty and resin acids and BOD. High loadings were apparently reflected also in the lower percentage removal of the toxic compounds in the two oxygen-activated sludge systems studied.

Large reductions in concentrations of the toxicants were observed following precipitation processes. Systems studied included lime precipitation and tertiary treatments employing alum.

Reverse osmosis demonstrated essentially complete rejection of fatty and resin acids. Performance of pilot ultrafiltration units was either good or marginal, apparently depending upon the type of membrane used. Although chloroform contents of the samples were affected minimally by ultrafiltration, they underwent reductions of from 88 to 98% in all of the other treatment systems studied.

This report was submitted in fulfillment of Grant No. R-803525-04 by The Institute of Paper Chemistry under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period August 6, 1976 to November 9, 1977, and work was completed as of August 11, 1977.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

bleach toxicants	-- trichloroguaiacol, tetrachloroguaiacol, epoxystearic acid, dichlorostearic acid, monochlorodehydroabietic acid, dichlorodehydroabietic acid
BOD	-- five-day biochemical oxygen demand
°C	-- degrees Centigrade
Clar.	-- clarifier (in Fig. 9, 13)
cm^3	-- cubic centimeter
Conc.	-- concentrator (in Fig. 13)
day^{-1}	-- food to microorganism ratio, lb BOD/day/lb MLSS
EPA	-- Environmental Protection Agency
°F	-- degrees Fahrenheit
Floc.	-- flocculator (in Fig. 13)
ft	-- feet
ft/sec	-- feet per second
$gal/day\text{-}ft^2$	-- gallons per day per square foot
GC/MS	-- gas chromatography/mass spectrometry
gpm	-- gallons per minute
ha	-- hectares
He	-- helium
in.	-- inch
Institute	-- The Institute of Paper Chemistry; Appleton, Wis.
kg	-- kilogram
kg/cm^2	-- kilograms per square centimeter
kw	-- kilowatt
lb	-- pound
m	-- meter
m^2	-- square meters
m^3/day	-- cubic meters per day
M gpd	-- million gallons per day
µg	-- microgram
ml/g	-- milliliter per gram
MLSS	-- mixed liquor suspended solids
µm	-- micrometers
NCASI	-- National Council of the Paper Industry for Air and Stream Improvement
NHB	-- North Holding Basin — Mill 13
NSSC	-- neutral sulfite semichemical
PCB	-- Primary Control Basin — Mill 13
percentage removal	-- 100 (raw concentration-final concentration)/raw concentration

ppb	-- parts per billion	
ppm	-- parts per million	
psi	-- pounds per square inch	
RO	-- reverse osmosis	
SHB	-- South Holding Basin — Mill 13	
SS	-- suspended solids	
U.B.	-- unbleached	
UF	-- ultrafiltration	
C	-- chlorination	Stages of bleaching sequence
E	-- caustic extraction	
H	-- hypochlorite	
D	-- chlorine dioxide	
O	-- oxygen	

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SECTION 1

INTRODUCTION

Organic compounds exhibiting a toxic effect on fish have long been known to exist in pulping and bleaching wastes. Types of compounds found to be present in pulp mill effluents and to contribute to effluent toxicity include resin acids, chlorinated resin acids, unsaturated fatty acids, other acidics (epoxystearic acid, dichlorostearic acid), and chlorinated phenolics (1-4). The toxicity of these compounds and of mill effluents has been studied extensively in Canada; this work was recently reviewed by Walden and Howard (5) and Leach and Thakore (6). The current investigation has been prompted by the increasing concern with toxic materials in the United States.

Recent research has revealed that these toxic, wood-derived compounds are biodegradable to varying degrees (7) and that they can be removed from effluents by biological and physicochemical detoxification processes (8,9). It became of interest, therefore, to learn the extent to which these materials are degraded or removed in several pilot and mill-scale waste treatment systems presently operating in different locations throughout the United States. Waste treatments selected for study were membrane processes (reverse osmosis and ultrafiltration), precipitation processes originally developed for color removal (alum and lime treatments), air-activated sludge, oxygen-activated sludge, and aerated lagoons. In mills where these secondary and tertiary processes are preceded by primary clarification, the effect of the primary treatment on the compounds of interest was also studied. This reported work relates only to the presence, quantity, and fate of the specific compounds listed below; no attempt was made to develop a cause-effect relationship in receiving waters.

Resin acids:

- Abietic
- Dehydroabietic
- Isopimaric
- Pimaric

Chlorinated resin acids:

- Monochlorodehydroabietic
- Dichlorodehydroabietic

Unsaturated fatty acids:

- Oleic
- Linoleic
- Linolenic

Unsaturated fatty acid derivatives:

9,10-Epoxystearic acid
9,10-Dichlorostearic acid

Chlorinated phenolics:

3,4,5-Trichloroguaiacol
3,4,5,6-Tetrachloroguaiacol

Halomethane:

Chloroform

SECTION 2

CONCLUSIONS

Nearly all of the waste treatment systems studied in this investigation removed essentially all of the compounds of interest quite effectively. Greater than 90% removal of fatty and resin acids was achieved in eight out of thirteen mill-scale treatment facilities studied. Only three mills had detectable amounts (>40 ppb) of bleach toxicants (chlorinated fatty acids, resin acids, and guaiacols) in their final effluents. Amounts of chloroform in final mill effluents (8-75 ppb) were in the range that has been reported for some municipal drinking waters (2-152 ppb).

Very little removal of fatty and resin acids or bleach toxicants occurred during primary clarification. These compounds were apparently not associated with the suspended solids removed.

Raw effluents from the two sulfite mills in the program contained lower levels of fatty and resin acids than raw effluents from the kraft mills. Amounts of bleach toxicants in the sulfite mill raw effluents were near or below the detection limit. Concentrations of all of these compounds were effectively reduced during secondary treatment.

Most lagoons and air-activated sludge systems achieved high percentage removals of fatty and resin acids from kraft mill effluents. Systems which exhibited poorer performance received high loadings of BOD and of fatty and resin acids. High loadings of fatty and resin acids appeared also to have influenced the lower percentage removal of these toxic compounds in the two oxygen-activated sludge facilities studied.

The relative ability of biological waste treatment processes to degrade bleach toxicants paralleled their ability to remove fatty and resin acids. In each case, percentage removal of the bleach toxicants was less than the percentage removal of their unchlorinated analogs.

The one lime precipitation system studied demonstrated a percentage removal of fatty and resin acids that greatly exceeded its percentage removal of BOD. Laboratory-scale alum precipitations, used as tertiary treatments, reduced fatty and resin acids and bleach toxicants to below detection limits.

Reverse osmosis demonstrated essentially complete rejection of fatty and resin acids. Rejection of bleach toxicants by a pilot ultrafiltration system with a dynamic membrane was good. An ultrafiltration unit with a synthetic polymer membrane was much less effective.

SECTION 3

RECOMMENDATIONS

Investigations into the production and fate of potentially toxic compounds emanating from pulp and paper mills should be continued. In some instances, in-plant waste control systems applied to specific process streams within the mill might be considered a desirable means of removing these wood-derived compounds from raw wastes and ultimately from effluents. To assure efficient use of in-plant control facilities, the production of the compounds of interest by the various potential sources within the mill should be investigated and documented. Among specific streams to be analyzed in a recommended future survey are wet barking wastes, condensates, machine white water, and effluents from screen rooms, decker, chlorination, and caustic extraction. From such a study involving several mills would be developed an account of the contribution of the mills' unit processes to the total load of wood-derived toxicants in their raw wastes.

SECTION 4

PROGRAM DESIGN

Mills invited to participate in this study were selected and initially contacted by the Project Officer. In many cases these mills had conducted or were conducting projects on their waste treatment facilities under partial EPA sponsorship. The mills which participated in this project (listed by code number), and their pulping process, location, and waste treatment process studied are shown in Table 1.

TABLE 1. PARTICIPATING MILLS

Mill no.	Pulping process	Location	Waste treatment process
1	Semichemical	Northern midwest	Reverse osmosis
2	Bleached kraft	Southeast	Ultrafiltration
3	Bleached kraft	South	Ultrafiltration
4	Unbleached and bleached kraft	East	Oxygen-activated sludge
5	Unbleached kraft	South	Oxygen-activated sludge and alum treatment
6	Unbleached kraft and semichemical	South	Lime treatment
7	Bleached sulfite	East	Activated sludge
8	Bleached kraft	Northwest	Activated sludge
9	Unbleached kraft and semichemical	South	Aerated lagoon
10	Bleached sulfite	Northwest	Aerated lagoon
11	Bleached kraft	Northern midwest	Aerated lagoon
12	Bleached kraft	East	Activated sludge
13	Bleached kraft	West	Aerated lagoon
14	Unbleached kraft	Northwest	Aerated lagoon
15	Bleached kraft	South	Aerated lagoon and alum treatment

Analytical methodology necessary for the conduct of this project existed before the project began. However, it was essential to reaffirm, as shown later in this report, that these methods could be used successfully on the types of samples analyzed in this investigation. Where instrumentation needed for a determination was not available at the Institute, the determination was performed by a subcontractor. Thus, the chloroform determinations were run at the West Coast Regional Center of the National Council of the Paper Industry for Air and Stream Improvement (NCASI), and determinations of the other chlorinated compounds and epoxystearic acid were performed by Calgon Corporation. For most mills in this program, shipping time and sample instability precluded sending samples to Appleton for BOD determinations. Consequently, BOD's were run at the participating mills.

Although all of the compounds of interest were determined in effluents from mills with bleaching, only the unchlorinated compounds were sought in effluents from mills without bleaching. Most of the toxicity in first caustic extraction stage bleach effluent has been reported to result from chlorinated resin and fatty acids, chloroguaiacols, and epoxystearic acid (4). Therefore, only these compounds, and not their unchlorinated analogs, were determined in caustic extraction stage effluents in this project.

As noted later in the report, techniques had to be tested for preserving and shipping samples containing the compounds of interest. In order to characterize properly most of the facilities under study, samples were taken over periods of 8-12 hours and in three rounds of sampling separated by two-week periods. The character of some sample streams permitted use of alternate schedules, and in some cases sampling was delayed by mill upsets and equipment problems. In a few instances extra samples were taken which were of particular interest to the participating mill. Samples from Mill 7 were taken and analyzed in duplicate.

The design and conduct of this investigation have been devoted exclusively to the determination of the compounds of interest in the waste treatment facilities under study. Conclusions regarding the environmental impact of these compounds on the receiving streams must await the attention of other investigators.

SECTION 5

DEVELOPMENT OF ANALYTICAL PROCEDURES

FATTY AND RESIN ACIDS

The method used for determining fatty and resin acids has been described in two NCASI bulletins (10, 11). The earlier of these reports was based on research conducted in this laboratory under NCASI sponsorship. In the most recent bulletin a liquid chromatographic method is described for the separation of neutral compounds from methyl esters before gas chromatographic (GC) analysis. This technique was used frequently in the present analysis of mill effluents. The completeness of separation was evaluated by passing a solution containing known quantities of oleic, abietic, and isopimaric acid through the column. Recoveries of 94 to 102 percent were obtained. A typical GC curve of an untreated mill effluent is shown in Fig. 1.

The method without the separation of the neutrals was tested by spiking mill effluents with oleic and isopimaric acid, and the recoveries were determined (Table 2).

TABLE 2. RECOVERY OF FATTY AND RESIN ACIDS FROM MILL EFFLUENTS

	Oleic acid (ppm)					Isopimaric acid (ppm)				
Sample	Present	Added	Total present	Total found	%	Present	Added	Total present	Total found	%
Pulp mill effluent	9.4	17.1	26.5	25.4	96	3.5	8.7	12.2	12.1	99
Lagoon effluent	3.68	1.71	5.39	5.38	100	1.78	0.87	2.65	2.25	85

The extensive studies by the Institute (10) and NCASI (11) on the determination of fatty and resin acids were considered adequate to validate this procedure and avoid any further testing.

BLEACH PLANT TOXICANTS

In the analysis of bleach plant effluents, the following compounds were to be measured:

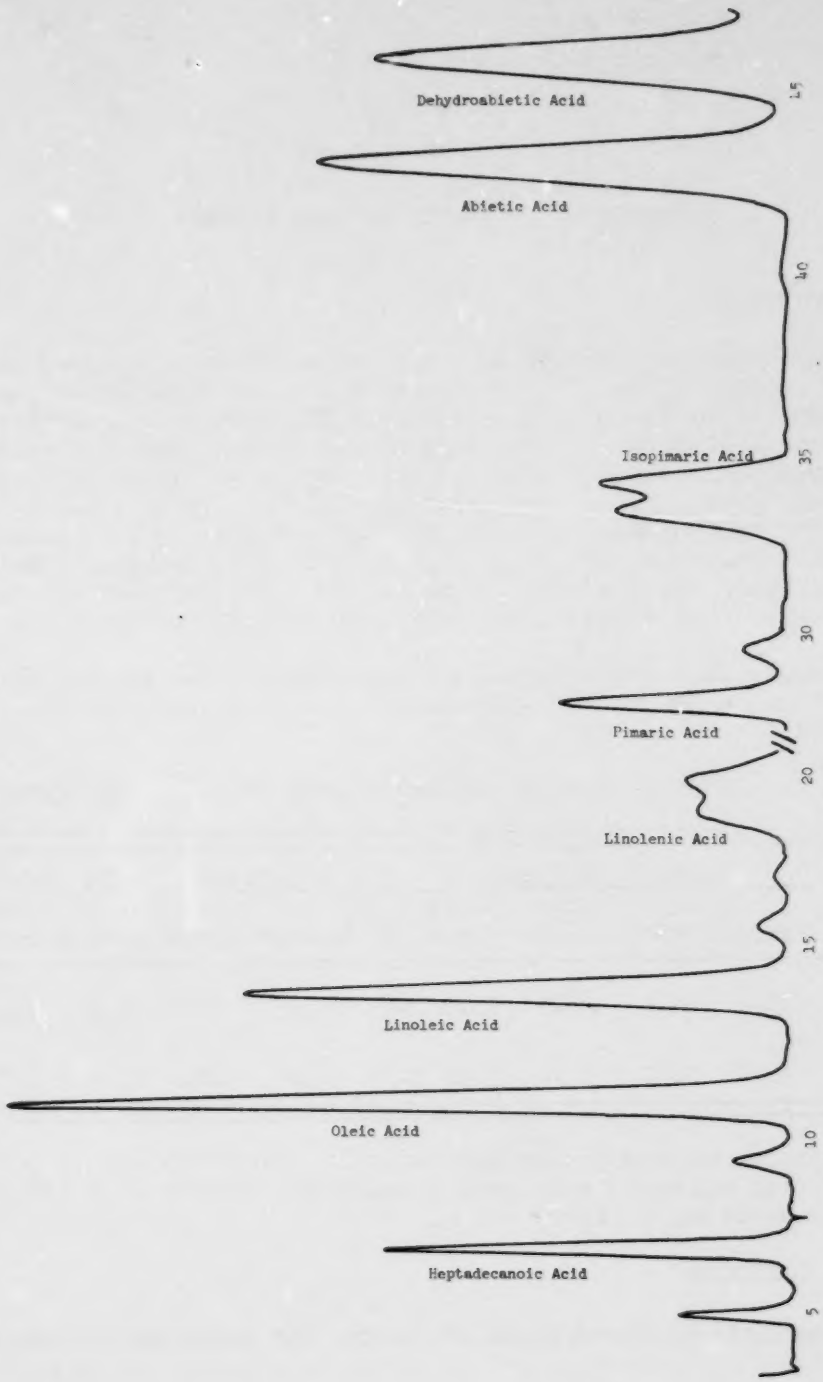


Figure 1. Gas chromatogram of U.B. kraft effluent.

3,4,5-Trichloroguaiacol

3,4,5,6-Tetrachloroguaiacol

9,10-Epoxystearic acid

9,10-Dichlorostearic acid

Monochlorodehydroabietic acid

Dichlorodehydroabietic acid

Methods for the isolation and measurement of these materials appeared in a report by B. C. Research for the Canadian Department of the Environment (4). In that report the compounds were isolated from kraft mill caustic extraction effluents by adsorption on XAD-2 resin. The separation and measurement were accomplished by GC analysis of the methylated materials. Gas chromatography-mass spectrometry (GC/MS) was used for confirmation. That report included an investigation of solvent extraction as a means of isolation of the toxicants, but quantitative removal of all the compounds was not achieved. Further work in this area was recommended.

A study of the efficiency of extraction with anhydrous ethyl ether in this laboratory showed complete separation when the aqueous samples were extracted at pH 3, as illustrated in Table 3. The extracts were analyzed by gas chromatography using a flame ionization detector. Quantitation was achieved by the use of an internal standard (heptadecanoic acid) and comparison of the areas. Detector factors were established and applied in the calculations. Authentic samples of these compounds were supplied by B. C. Research and NCASI. Dichlorostearic acid and trichloroguaiacol were prepared in our laboratory according to the procedures used in the B. C. Research report (4, 12). Extractability was determined by adding known quantities of the compounds to distilled water and extracting with ethyl ether at various acid concentrations. A bleached kraft mill effluent was spiked with known quantities of the compounds and extracted at the optimum pH to verify recovery from a typical mill sample. The effluent did not contain concentrations of bleach plant toxicants that could be detected with a flame ionization detector.

The compounds were readily separated (Fig. 2) using the following conditions for the gas chromatography:

Column: 1.83 x 0.0032 m (6 ft x 1/8 in.) stainless steel, containing 3% OV-17 on Supelcoport 80/100
Column temp.: 150-250°C at 3°/min
Injector temp.: 225°C
Detector temp.: 275°C
Detector: flame ionization
Carrier gas: He at 30 cm^3/min

The methylated extracts of the mill samples were analyzed by limited mass reconstructed gas chromatography in an outside laboratory. A description of this analysis may be found in the methods section of this report.

TABLE 3. EXTRACTABILITY OF BLEACH PLANT TOXICANTS

Compound	Distilled Water (250 cm³)												Bleached kraft lagoon effluent, 250 cm³ at pH 3		
	pH - 2			pH - 3			pH - 4			pH - 5					
	Add (mg)	Found (mg)	%	Add (mg)	Found (mg)	%	Add (mg)	Found (mg)	%	Add (mg)	Found (mg)	%	Add (mg)	Found (mg)	%
Trichloroguaiacol	0.840	0.835	99	0.840	0.731	87	0.840	0.723	86	0.840	0.722	86	0.86	0.88	102
Tetrachloroguaiacol	0.824	0.813	99	0.824	0.844	102	0.824	0.773	94	0.824	0.791	96	0.89	0.90	101
Epoxystearic acid	0.840	0.839	100	0.840	0.76	90	0.840	0.830	99	0.840	0.773	92	0.86	0.86	100
Dichlorostearic acid	Not Available for this Determination												1.22	1.00	82
Monochloro-dehydroabietic acid	0.848	0.805	95	0.848	0.823	97	0.848	0.784	92	0.848	0.777	92	0.73	0.78	107
Dichloro-dehydroabietic acid	0.832	0.828	100	0.832	0.800	96	0.832	0.772	93	0.832	0.793	95	0.80	0.75	94

Figure 2. Gas chromatogram of bleach plant toxicants.

CHLOROFORM

The chloroform determinations were performed by the NCASI laboratory in Corvallis, Oregon. They used an extraction procedure similar to the method of Richard and Junk (13) for the analysis of the mill effluents. The extracts were analyzed on a gas chromatograph equipped with an electron capture detector. A microcoulometric halide detector was used to verify the composition of some of the peaks. The NCASI laboratory reported an average recovery of 98% (88-119) when spiked mill effluents were analyzed. Detection limits were not determined, but a concentration of 1 μg/1000 cm^3 could be easily measured.

STABILITY OF FATTY AND RESIN ACIDS

A preliminary study was conducted to determine the best practical conditions for preserving the samples during shipment from the mill to the laboratory. Losses have been observed during storage even when the samples are adjusted to pH 11 and kept refrigerated (11). A quantitative evaluation of the losses was considered necessary before proceeding with any of the sampling.

The samples for this study were obtained from a typical unbleached kraft mill. Samples from two sites in the mill's sewer system were collected by a one-time grab method. The samples represented an untreated effluent which was taken from the pulp mill's sewer and a treated effluent which came from the outfall of the aerated lagoon.

In the initial study, the samples were adjusted to pH 11 and stored in the refrigerator at 3°C. The adjusted effluents were contained in 500 cm^3 amber glass bottles fitted with Teflon-lined screw caps. The bottles were filled to the top to eliminate any air. (Most of the bottles contained about a 1 cm^3 air space after standing for 4-5 days.) Duplicate analyses were made on the unaged samples and single determinations were made after 5 and 10 days of storage. Results in Table 4 indicate that losses of fatty and resin acids were insignificant during 10 days' storage at 3°C and pH 11.

The difficulty of keeping samples refrigerated during shipment by air freight prompted a further investigation involving the stability of the samples when stored at ambient temperature (22°C). Another set of samples was collected from the same sampling points. Duplicate samples were analyzed initially and after 4 and 10 days' storage.

The data in Table 5 suggest that the treatment system was generating fatty and resin acids rather than removing them. Apparently the grab sample from the pulp mill sewer was a poor representation of this source. The outfall of the lagoon was not typical either due to the extremely low temperature of -29°C (-20°F) on the day the samples were taken. Nevertheless, in spite of nonrepresentative sampling, the data in Table 5 suggest that fatty and resin acid contents of effluents would not be significantly altered during shipment at ambient temperature and pH 11.

Dichloromethane, considered for possible use as a preservative, was added to separate aliquots of the above samples at a concentration of 5 cm^3 per

TABLE 4. ANALYSIS OF EFFLUENTS STORED AT 3°C AND pH 11

Acid	Pulp Mill Sewer (ppm)				Aerated Lagoon Outfall (ppm)			
	Unaged	(Av.)	5 Days	10 Days	Unaged	(Av.)	5 Days	10 Days
Oleic	9.28 - 9.46[2]	9.37	9.44	9.36	3.68 - 3.68	3.68	4.02	4.27
Linoleic	8.22 - 8.34	8.34	8.50	9.03	2.32 - 2.24	2.28	2.43	2.48
Linolenic	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pimaric	N.D.[1]	N.D.	N.D.	N.D.	N.D.		N.D.	N.D.
Isopimaric	3.47 - 3.53	3.50	3.82	3.95	1.83 - 1.72	1.78	1.65	1.79
Abietic	6.70 - 6.74	6.72	7.33	7.07	1.88 - 2.14	2.01	1.80	2.48
Dehydroabietic	6.04 - 6.54	6.29	5.99	5.92	1.60 - 1.77	1.68	1.21	1.96
Total		34.2	35.1	35.3		11.4	11.1	13.0

[1]N.D. No pimaric acid was available at this time, so the determination was not made.

[2]Duplicate determinations.

TABLE 5. ANALYSES OF EFFLUENTS AT 22°C AND pH 11

Acid	Pulp Mill Sewer (ppm)						Aerated Lagoon Outfall (ppm)					
	Unaged	(Av.)	4 Days	(Av.)	10 Days	(Av.)	Unaged	(Av.)	4 Days	(Av.)	10 Days	(Av.)
Oleic	0.97 - 0.74	0.86	0.76 - 0.76	0.76	0.76 - 0.70	0.73	5.49 - 5.49	5.49	5.93 - 6.02	5.98	6.21 - 6.24	6.22
Linoleic	0.72 - 0.61	0.66	0.73 - 0.64	0.68	0.67 - 0.64	0.66	3.46 - 3.38	3.42	3.37 - 3.33	3.35	2.64 - 2.76	2.70
Linolenic	0.04 - 0.01	0.02	0.05 - 0.02	0.04	0.04 - 0.01	0.02	0.07 - 0.08	0.08	0.10 - 0.12	0.10	<.02	<.02
Pimaric	1.58 - 1.63	1.60	1.93 - 1.51	1.72	1.54 - 1.67	1.60	2.76 - 2.75	2.76	2.61 - 2.78	2.70	2.80 - 3.08	2.94
Isopimaric	1.20 - 1.17	1.18	1.20 - 1.13	1.16	1.25 - 1.34	1.30	5.14 - 4.92	5.03	3.79 - 4.49	4.14	4.97 - 5.40	5.18
Abietic	1.18 - 0.99	1.08	1.19 - 0.93	1.06	1.28 - 1.41	1.34	2.44 - 2.30	2.37	2.38 - 2.63	2.50	2.16 - 2.14	2.15
Dehydroabietic	1.16 - 0.96	1.06	1.12 - 0.80	0.96	0.93 - 1.41	1.17	0.98 - 0.93	0.96	0.80 - 0.91	0.86	0.98 - 1.00	0.99
Total (av.)		6.46		6.38		6.82		20.1		19.6		20.2

100 cm^3 effluent. No pH adjustment was made, although the pulp mill sewer was at pH 10.5 and the lagoon outfall was at pH 8.3. The fatty and resin acid concentrations decreased about 25% after 10 days' storage in a refrigerator. Further efforts to develop dichloromethane as a preservative were abandoned.

STABILITY OF BLEACH PLANT TOXICANTS

The stability of certain toxic compounds from bleach plants during storage was determined under the same conditions that were found to be satisfactory for fatty and resin acids (pH 11, 22°C). Adjustment of the pH to 3 for shipping was also investigated.

A sample of the secondary effluent from a typical bleached kraft mill was obtained for testing. The quantities of toxicants found in the initial analysis of the secondary effluent and the bleach plant sewer were too low to be useful in an evaluation of their stability. The use of an electron capture detector to improve the sensitivity and specificity was considered, but the initial trials indicated the need for a significant amount of exploratory work to make this workable. Spiking of the effluent with quantities that could be determined with a flame ionization detector was the most practical method of completing this study. The concentrations added were much larger than would normally be found in effluents, but it was hoped that general trends could be established. Samples of the secondary effluent were spiked with known quantities of the toxicants, adjusted to pH 3 and pH 11, and stored at room temperature (22°C) for various periods of time. The spiked sample was analyzed in duplicate without aging, and single determinations were made on samples aged 4 and 7 days.

Results shown in Table 6 demonstrate that the shipping conditions proposed for the samples to be analyzed for fatty and resin acids were also adequate for the bleach plant toxicants.

TABLE 6. STABILITY OF BLEACH PLANT TOXICANTS

Compound	Unaged (ppm) (Duplicates)	Unaged (ppm) (Av.)	4 Day Storage (ppm) pH - 3	4 Day Storage (ppm) pH - 11	7 Day Storage (ppm) pH - 3	7 Day Storage (ppm) pH - 11
Trichloroguaiacol	3.44 - 3.56	3.50	3.28	3.36	3.28	3.64
Tetrachloroguaiacol	3.52 - 3.64	3.58	3.36	3.28	3.24	3.72
Epoxystearic acid	3.48 - 3.40	3.44	0.08	2.92	0.72	2.08
Dichloro-stearic acid	4.12 - 3.96	4.04	3.96	4.44	3.72	4.96
Monochloro-dehydroabietic acid	3.08 - 3.20	3.14	3.00	3.24	2.80	3.44
Dichloro-dehydroabietic acid	3.04 - 2.96	3.00	3.00	3.20	2.68	3.36
Total		20.70	16.68	21.44	16.44	21.20

SECTION 6

PROCEDURES USED IN INVESTIGATION

SAMPLING AND SAMPLE PRESERVATION

The sampling was carried out by mill personnel. Each mill was instructed as to the purpose of each sample so that a suitable sampling point could be established. The specific sampling points for each mill are indicated on the waste water treatment system diagrams.

To achieve the goal of the project, it was important to have the output of a system representative of the input. Continuous sampling over an 8-12 hour period was recommended. Flow-proportional automatic samplers were used, when available. The composites were refrigerated during sampling, if possible. The samples sent to the Institute were adjusted to pH 11 with 10% sodium hydroxide solution and kept cool (3°C) until shipped.

Samples for determination of bleach plant toxicants and fatty and resin acids were placed in 500-cm^3 (pint) amber bottles. The bottles were filled to within 1 cm of the top with the sample at ambient temperature (22°C) (72°F). Screw caps fitted with Teflon-faced inserts were used to seal the bottles.

Samples for chloroform determination, with no pH adjustment, were placed in 125-cm^3 (4-oz) bottles. The bottles were filled to the top to eliminate any air and sealed with Teflon-lined screw caps.

The bottles were placed in polyfoam shipping cartons and shipped immediately by air freight. The samples for the chloroform determination were shipped directly to the NCASI laboratory in Corvallis, Oregon.

Each mill was supplied with the required number of bottles, liners, and shipping cartons to collect three sets of samples. The bottles were cleaned by washing with a detergent, and rinsing with hot water, distilled water, and finally, acetone. After the bottles were allowed to air dry, they were labeled, capped, and sent to the participating mills. Specific sampling and shipping instructions were included.

DETERMINATION OF FATTY AND RESIN ACIDS

Solvent Extraction

The entire sample (500 cm^3) was transferred to an Erlenmeyer flask. A 250-cm^3 aliquot was removed for analysis. The sample was thoroughly mixed

during the removal of the aliquot to ensure even distribution of any solids. A measured amount (100 cm^3) of anhydrous ethyl ether was used to rinse the sample bottle and a proportional amount (50 cm^3) was combined with the ether used for the extraction.

The sample was acidified to pH 3.0 with 10% sulfuric acid. A pH meter was used for this adjustment. The acidified sample was transferred to a separatory funnel (500-cm^3) and 2.0 cm^3 of a heptadecanoic acid solution was added as an internal standard. The internal standard solution was prepared by dissolving a weighed amount of acid in a quantity of methanol to produce a concentration of one milligram per cubic centimeter. This standard was freshly prepared each day.

The aqueous sample was extracted by shaking vigorously with 70 cm^3 of ethyl ether for about 20 seconds. The ether layer was transferred to a second separatory funnel (250-cm^3) containing 10 cm^3 of acidified water. The extraction was repeated with two 50-cm^3 portions of ether. All the ether extracts and any emulsified materials (which frequently formed at the interface) were transferred to the second funnel. When the emulsion persisted in the second funnel, the combined extracts were centrifuged to separate the layers.

The clear ether layer was transferred to an Erlenmeyer flask, and a few grams of anhydrous sodium sulfate were added to remove the water. The ether was removed on a rotary evaporator at 30°C. The evaporation was carried on until the sample <u>just</u> reached dryness. The residue was immediately dissolved in 8 to 10 cm^3 of ether-methanol (9:1).

<u>Preparation of Methyl Esters</u>

The methyl esters of the acids were formed by the addition of a fresh ether solution of diazomethane. The diazomethane was generated from a mixture of 3.5 cm^3 of Carbitol, 1.2 cm^3 of 37.5% potassium hydroxide and 2.2 grams of Diazald (Aldrich Chemical Co.). The Carbitol, potassium hydroxide, and one cm^3 of ether were placed in a 50-cm^3 distilling flask having a long side arm which terminated below the surface of 15 cm^3 of ether in an Erlenmeyer flask (50-cm^3). The receiving flask was placed in an ice bath and the distilling flask in a water bath at 60-70°C. A solution containing 2.2 grams of Diazald in 15 cm^3 of ether was introduced into the generator via a dropping funnel attached to the top of the distilling flask. The Diazald solution was added at a uniform rate over a two-minute period. The dropping funnel was finally rinsed with 5 cm^3 of ether.

The extracts were methylated immediately by adding the diazomethane dropwise until a definite yellow color persisted. (When the extract was colored so that the endpoint could not be distinguished, a weighed amount of heptadecanoic acid equal to the weight of the extract was titrated with diazomethane to give a rough estimate of the volume required for complete methylation.) After 10-15 minutes, the diazomethane and solvent were removed on a rotary evaporator at 30°C. The extract was taken to <u>near</u> dryness and redissolved in 1 cm^3 of n-hexane.

Separation of Methyl Esters from Neutrals

The presence of certain non-acidic compounds in some of the samples made the gas chromatographic analysis difficult due to the large number of peaks which inhibited good resolution of the acids to be measured. In such cases the methyl esters were separated from the neutrals by column chromatography.

A glass column 200 mm long with an inside diameter of 6 mm was packed with a 40-mm layer of silica gel plus a 10-mm layer of anhydrous sodium sulfate. The silica gel was a product of Davison Chemical, Baltimore, Maryland, grade 950, 60-200 mesh, No. 950-08-08-226. The silica gel was activated at 130°C and stored along with the sodium sulfate at 130°C. Columns were packed hot to avoid deactivation at room temperature.

One cm^3 of hexane was passed through the column followed by 0.3 cm^3 of the hexane solution of the methyl esters. Azulene (50 µl of a hexane solution containing 1 µg/µl) and Sudan I (10 µl of a hexane solution containing 10 µg/µl) were added to the methyl ester aliquot to serve as indicators in the separation. The esters were loaded onto the column when the level of the hexane (1 cm^3) reached the top of the sodium sulfate. A solvent composed of hexane and ethyl ether (95+5) was used to separate the methyl esters which were contained in the fraction between the start of the elution of the azulene and the start of the elution of Sudan I.

The fraction containing the methyl esters was concentrated on a rotary evaporator (30°C) to about 0.3 cm^3.

Gas Chromatographic Analysis

A Becker Model 417 gas chromatograph was used for the separation of the methyl esters (Fig. 1). The area measurements were made with a Disc integrator on a Honeywell Electronik 16 recorder. The use of this type of integrator made it necessary to buck out the increased background after programming. (Note break in curve, Fig. 1.)

The following conditions were used for the GC separation:

Column: 1.83 x 0.0032 m (6 ft x 1/8 in.) stainless steel containing 10% EGSS-X on Gas Chrom P, 100/120
Column temperature: 170°C for 22 minutes, Program 10°C/min to 200°C
Injector temperature: 200°C
Detector temperature: 235°C
Detector: flame ionization
Carrier gas: He at 30 cm^3/min
Volume injected: 3-4 µl

Calculations

$$\frac{\text{Area of acid x mg of internal std. x 1000}}{\text{Area of internal std. x ml of sample}} = \text{mg/l or ppm}$$

DETERMINATION OF BLEACH PLANT TOXICANTS

Solvent Extraction

The sample was extracted according to the procedure used for fatty and resin acids except for the quantity of heptadecanoic acid added as an internal standard. A solution containing 20 $\mu g/cm^3$ of heptadecanoic acid was prepared, and exactly 2.0 cm^3 was added to each 250 cm^3 sample.

Preparation of Methyl Esters and Ethers

The method reported for fatty and resin acids was followed. The time allowed for the reaction with diazomethane was increased from 10-15 minutes to 30 minutes.

The methyl esters and ethers were dissolved in one cm^3 of hexane and stored in a sealed ampule.

GC/MS Analysis

The toxicants in the methylated extracts were identified and measured by limited mass reconstructed gas chromatography. The analyses were performed by the Calgon Corporation, Water Management Division, Box 1346, Pittsburgh, Pa.

The samples and standards were analyzed using the GC/MS conditions listed below:

Column: 1.52 m x 2.0 mm ID glass, packed with 3% OV-17 on 100/120 mesh Gas Chrom Q
Column temperature: 135°C to 230°C at 2°C/minute
Injector temperature: 240°C
MS inlet temperature: 240°C
MS analyzer pressure: 5×10^{-5} Torr
Mass range: 20 to 450 atomic mass units (less air)
Scan rate: 7 m sec/atomic mass unit
Multiplier voltage: 1800 volts
Electron energy: 70 electronvolts
Emission current: 0.5 milliamps
Preamp sensitivity: 10^{-7} amps/volt

Quantitation was by area comparison with the internal standard, heptadecanoic acid, using response factors based on standard solutions. The specific ions used for quantitative measurements were:

Heptadecanoic acid	– 74 m/e
Trichloroguaiacol	– 162
Tetrachloroguaiacol	– 276
Dichlorostearic acid	– 74
Epoxystearic acid	– 155
Monochlorodehydroabietic acid	– 43
Dichlorodehydroabietic acid	– 43

DETERMINATION OF CHLOROFORM

Five to ten cm^3 of effluent were extracted with 2.0 to 4.0 cm^3 of purified hexane. The hexane was purified by distillation, followed by passage through a column packed with activated alumina (MCB 9296 heated to 400°C).

A 15-cm^3 graduated glass-stoppered centrifuge tube was used for the extraction. The sample and hexane were shaken vigorously for 15 seconds and allowed to stand for a few minutes. The hexane layer was removed with a disposable pipet and stored in a small screw cap vial.

The extract was analyzed by injecting directly onto the GC column. Conditions for the gas chromatographic analysis are as follows:

Column: 4.6 x 0.003 m (15 ft x 1/8 in.) stainless steel containing 10% Carbowax 20 M on Gas Chrom Q, 100/120.
Column temperature: 70°C for 8 minutes, then programmed to 140°C at 6°C/min. A constant temperature of 95°C was used for samples that contained only chloroform.
Carrier gas: Nitrogen at 20 cm^3/min with detector make-up flow at 30 cm^3/min.
Detector: (1) Electron capture, Model 140A, Analog Technology Corp., constant current type.
(2) Microcoulometric halide detector.

Standards for gas chromatographic analyses were prepared by volumetrically adding chloroform to hexane.

SECTION 7

RESULTS OF ANALYSES

MILL 1

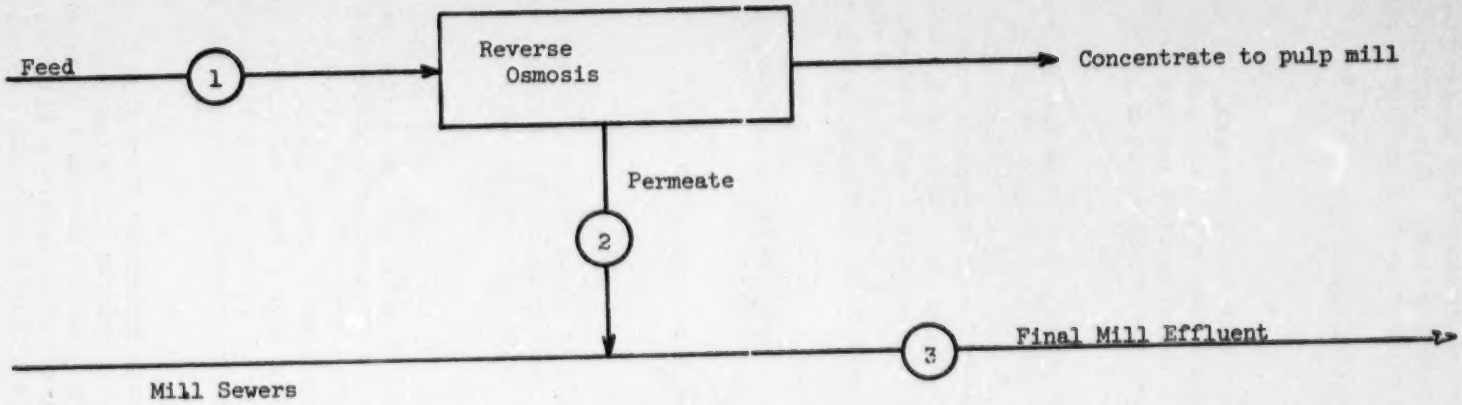
Mill 1, located in the northern midwest, produces about 272 metric tons/day (300 tons/day) of corrugating medium. About 181 metric tons/day (200 tons/day) of neutral sulfite semichemical pulp are produced from mixed hardwoods, primarily red oak, elm, and hard and soft maple. An additional 91 metric tons/day (100 tons/day) of pulp are produced by repulping kraft clippings.

The mill operates with an essentially closed white water system. Excess water is removed from the system by a commercial size reverse osmosis (RO) plant. Weak wastes from the white water system are fed to the RO unit and separated into uncontaminated water (permeate) and a concentrate of white water solubles which is returned to the countercurrent washing system in the pulp mill. Feed to the RO plant contains 4-6% dissolved solids consisting of wood extractives and sodium lignosulfonates; it also contains about 300 ppm suspended solids. This feed is supplied to the RO plant at a pH of 5.6-6.0, a pressure of 7.03 kg/cm^2 (100 psi) and a temperature of 60-65°C (140-150°F). Prior to entry into the RO equipment the feed is cooled to 38°C (100°F).

The RO system is comprised of 288 modules divided equally among six racks. Each module contains 18 porous tubes which are fiberglass, filament-wound, and resin bonded. The membrane, formed from cellulose acetate, is on the inner surface of the fiberglass tubes and provides 1.55 m^2 (16.7 ft^2) of membrane surface per 18-tube module.

Clarified process water feed flow, under conditions of full plant operation, is 0.341 m^3/min (90 gpm). Two feed pumps pressurize this to 31.6 kg/cm^2 (450 psi) before it combines with the recycled concentrate. The combined flows, 0.946 m^3/min (250 gpm) are boosted by the six recycle pumps to 42.2 kg/cm^2 (600 psi). This feed is supplied to the six module rack assemblies in parallel. After passage through the modules, a portion of the concentrate, 0.255 m^3/min (67.5 gpm), is returned to the pulp mill, and the remainder is recycled for combining with fresh feed. Permeate goes into the mill discharge to the river. Although the design flux of the system was 0.011 m^3/m^2-hr (6.65 gal/day-ft^2), the present flux is about 0.0085 m^3/m^2-hr (5 gal/day-ft^2).

For this investigation, samples were taken of reverse osmosis feed, permeate, and total mill effluent, as indicated in Fig. 3. RO feed and permeate



Sampling Points

1. Feed
2. Permeate
3. Final effluent

Figure 3. Mill No. 1 reverse osmosis system.

were sampled by taking a 200-ml grab every half hour for eight hours. Sampling of total mill effluent was done with a chain-driven bucket sampler which emptied into a container inside a refrigerator. This device took a constant volume, timed sample every 3.75 minutes over a 24-hour period.

Analytical data from Mill 1 are shown in Table 7.

MILL 2

Mill 2 is a bleached kraft mill located in the southeast. It produces 1206 metric tons/day (1330 tons/day) of pulp from about 60% softwood and 40% hardwood. Of particular interest in this investigation was the treatment of a portion of the mill's pine caustic extraction filtrate in a pilot ultrafiltration unit.

The ultrafiltration unit is sketched in Fig. 4. From the feed tank the caustic extract passed through a Kisco filter containing 0.76 m (30 in.) of Filter AG granular anhydrous aluminum silicate. Final prefiltration in a Broughton basket type filter removed suspended solids greater than 10 μm. Only one spiral wound module was used in this study. Area of the Abcor WRP No. 1 membrane was 3.72 m^2 (40 ft^2). This is a proprietary synthetic polymer membrane which permits the feed to have higher temperature and pH than allowed by cellulose acetate membranes. Concentrate was not recycled in this investigation.

Samples taken for this study included feed, prefiltered feed, concentrate, and permeate.

Analytical data for these samples are reported in Table 8.

MILL 3

This mill, located in the south, produces about 544 metric tons/day (600 tons/day) of bleached kraft pulp. Its bleaching sequence is CEHD. Of interest at this location is a pilot ultrafiltration unit operating on the mill's caustic extract.

The feed tank for the ultrafiltration (UF) unit is supplied with caustic extract from the bleaching of hardwood, softwood (pine), or a combination of both. This valving arrangement in the mill bleach plant is necessary in order to ensure a continuous flow of caustic extract in the event that one of the bleaching operations goes down. Concentrate from the UF unit is recycled back to the feed tank during the course of a run, and new caustic extract is added to the tank at the same rate as permeate leaves the system. This flow is diagrammed in Fig. 5. Fibers are removed from the feed with a 5 μm woven polypropylene fabric filter.

The ultrafiltration unit employs dynamic membranes formed on a ceramic tubular support. The membranes consist of a hydrous zirconium oxide bottom layer and a hydrous silicon oxide overlayer. Each tube has a diameter of 0.58 cm (0.23 in.). There are 19 tubes in a bundle having a filtration area of 0.11-0.13 m^2/bundle (1.2-1.43 ft^2/bundle). The UF unit has a total surface

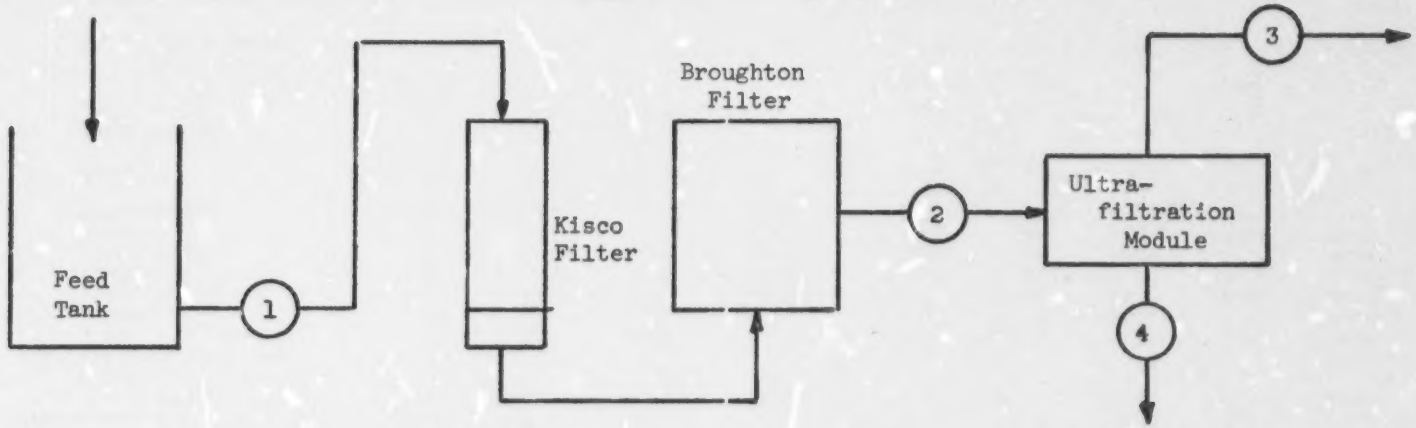
TABLE 7. MILL NO. 1 DATA

Mill No. 1; Location: Northern Midwest; Process: neutral sulfite semichemical

Wood Species: red oak, elm, hard and soft maple

Waste Treatment: reverse osmosis

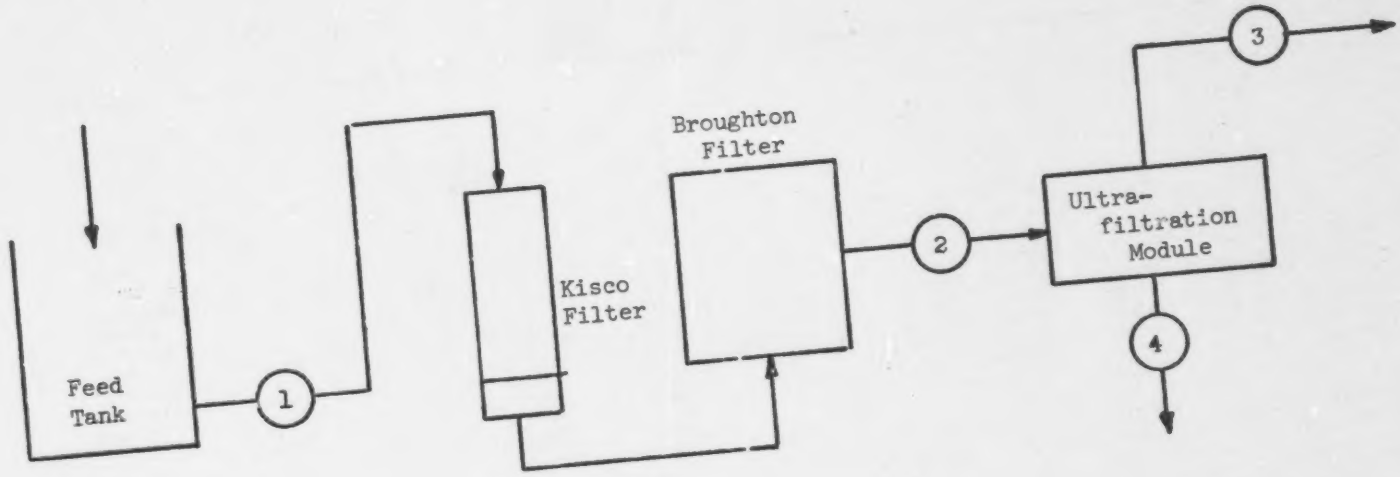
	Raw feed			Permeate			Total mill effluent		
Sampling date	4-5	4-26	5-10	4-5	4-26	5-10	4-5	4-26	5-10
BOD, ppm	11,200	10,200	10,600	1,100	1,320	1,170	52	51	41
Flow rate, m^3/min	0.33	0.33	0.33	0.028	0.028	0.028	4.84	3.79	3.90
(gpm)	(87)	(87)	(87)	(7.5)	(7.5)	(7.5)	(1280)	(1001)	(1030)
Production, metric tons/day	181.4	181.4	181.4	181.4	181.4	181.4	181.4	181.4	181.4
(short tons/day)	(200)	(200)	(200)	(200)	(200)	(200)	(200)	(200)	(200)
pH	5.7	5.8	5.5	4.0	4.3	3.8	7.8	7.8	7.8
Temperature, °C	37.8	37.8	37.8	37.8	37.8	37.8	22.2	29.4	31.7
(°F)	(100.0)	(100.0)	(100.0)	(100.0)	(100.0)	(100.0)	(72.0)	(85.0)	(89.0)
Fatty and resin acids, ppm									
Oleic	4.86	3.72	6.78	<0.02	0.05	<0.02	<0.02	0.02	<0.02
Linoleic	7.23	6.91	14.60	<0.02	0.03	<0.02	<0.02	0.02	<0.02
Linolenic	0.27	0.45	0.70	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pimaric	0.82	0.49	1.14	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Isopimaric	2.75	1.61	5.07	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Abietic	1.59	2.47	4.84	<0.02	0.04	<0.02	<0.02	0.04	<0.02
Dehydroabietic	2.62	2.89	4.62	<0.02	0.02	<0.02	<0.02	0.04	<0.02
Total	20.1	18.5	37.8	--	0.14	--	--	0.12	--
Daily loading									
kg/day	9.5	8.8	17.9	--	0.006	--	--	0.6	--
(lb/day)	(21.0)	(19.3)	(39.4)	--	(0.013)	--	--	(1.4)	--
kg/ton pulp	--	--	--	--	--	--	--	--	--
(lb/ton pulp)	--	--	--	--	--	--	--	--	--



Sampling Points

1. Raw Feed
2. Prefiltered
3. Concentrate
4. Permeate

Figure 4. Mill No. 2 ultrafiltration system.



Sampling Points

1. Raw Feed
2. Prefiltered
3. Concentrate
4. Permeate

Figure 4. Mill No. 2 ultrafiltration system.

TABLE 8. MILL NO. 2 DATA

Mill No. 2; Location: Southeast; Process: bleached kraft; Bleach Sequence: CEHEED

Wood Species: 60% softwood and 40% hardwood

Waste Treatment System: ultrafiltration

	Feed tank			Prefiltered			Concentrate			Permeate		
Sampling date	6-28	7-5	7-11	6-28	7-5	7-11	6-28	7-5	7-11	6-28	7-5	7-11
BOD, ppm	--	--	--	--	--	--	--	--	--	--	--	--
Flow rate, m^3/min	0.043	0.040	0.031	0.043	0.040	0.031	0.041	0.036	0.028	0.0022	0.0032	0.0027
(gpm)	(11.5)	(10.5)	(8.1)	(11.5)	(10.5)	(8.1)	(10.9)	(9.6)	(7.4)	(0.59)	(0.86)	(0.71)
Production, metric tons/day	--	--	--	--	--	--	--	--	--	--	--	--
(short tons/day)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)
pH	11.5	11.3	11.6	11.5	11.0	11.5	11.5	11.1	11.5	11.6	11.1	11.6
Temperature, °C	43.9	44.4	44.4	43.9	44.4	44.4	43.9	44.4	44.4	43.9	44.4	44.4
(°F)	(111)	(112)	(112)	(111)	(112)	(112)	(111)	(112)	(112)	(111)	(112)	(112)
Bleach plant products, ppm												
Trichloroguaiacol	3.52	5.24	4.81	3.07	5.04	3.59	3.60	4.50	3.38	0.652	2.20	2.02
Tetrachloroguaiacol	1.72	2.10	2.13	1.54	2.05	1.61	1.62	1.76	1.36	0.300	0.808	0.820
Epoxystearic acid	4.10	6.56	5.79	2.26	5.55	7.35	4.22	7.18	14.6	2.10	7.68	5.93
Dichlorostearic acid	0.564	0.824	0.972	0.284	0.728	1.00	0.404	0.736	1.52	0.100	0.492	0.516
Monochloro-dehydroabietic acid	0.152	0.404	0.160	0.100	0.252	0.116	0.084	0.360	0.924	0.132	0.212	0.128
Dichloro-dehydroabietic acid	0.292	0.596	0.516	0.196	0.576	0.412	0.276	0.556	1.24	0.328	0.752	0.460
Total	10.4	15.7	14.4	7.45	14.2	14.1	10.2	15.0	23.0	3.6	12.1	9.9
Chloroform, ppm	1.285	1.309	0.966	1.323	1.469	1.011	1.311	1.278	0.980	1.376	1.453	1.085

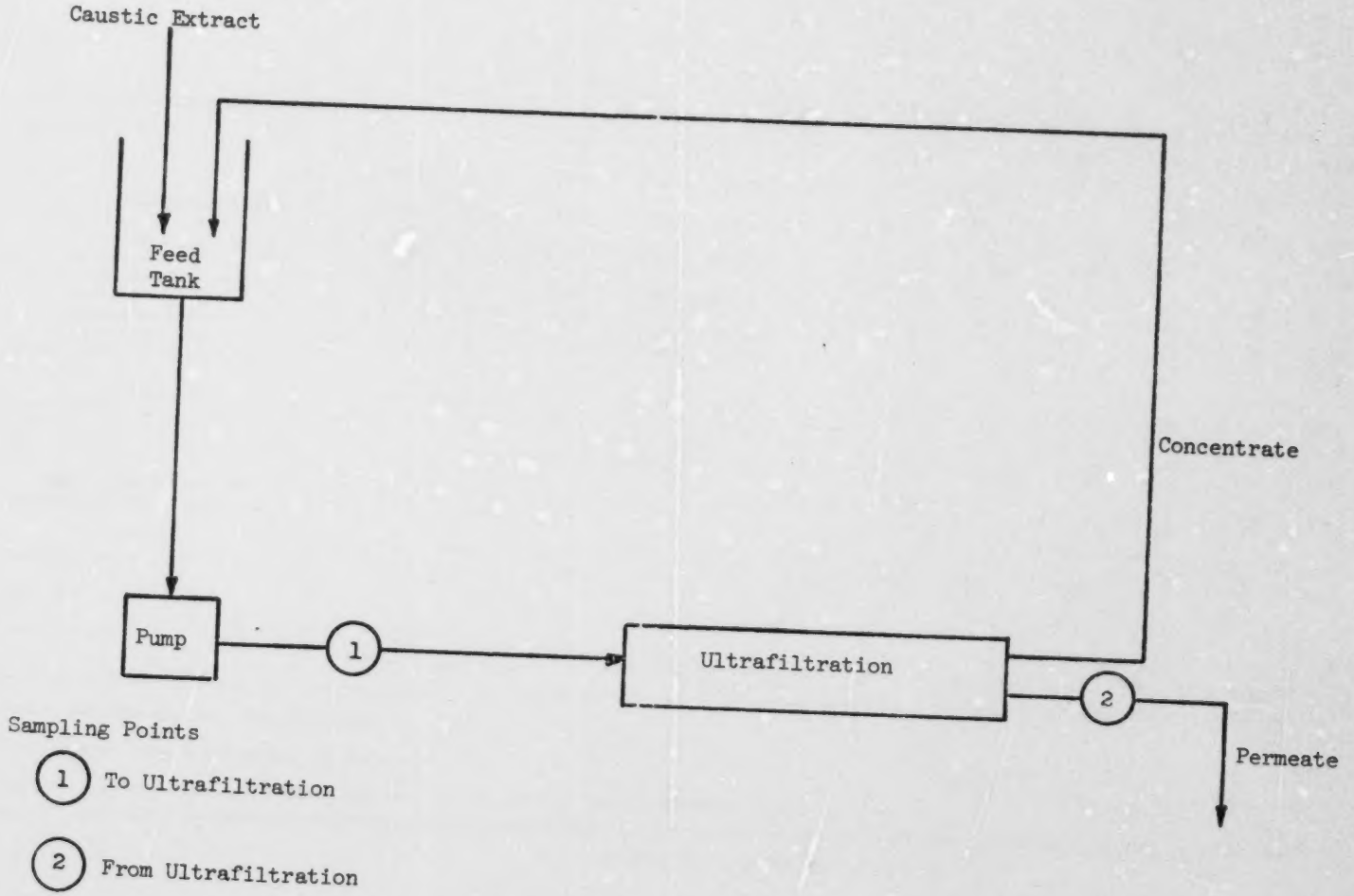


Figure 5. Mill No. 3 ultrafiltration system.

area of 1.12 m^2 (12.1 ft^2). Feed to the UF unit had a pH of 9.5-10.5 and a temperature of 46°C (115°F). Velocity of the feed across the membrane was 457 cm/sec (15 ft/sec) with a flow rate of 0.12 m^3/min (3.3 gpm). Permeate flow rate was 1.02 m^3/day (270 gal/day). Flux was 0.91 m^3/m^2-day (22.3 gal/day-ft^2). Pressures were 15.5 kg/cm^2 (220 psi) inlet and 7.03 kg/cm^2 (100 psi) outlet.

Samples of feed and permeate from the UF system were grab samples which were not composited over a time period. This was justified because the system was operating at close to steady state.

Analytical data for these samples are given in Table 9.

MILL 4

Mill 4 is an integrated kraft pulp and paper mill located on the east coast. Total production averages 860 metric tons/day (950 tons/day) of unbleached softwood kraft paper, corrugated medium, and linerboard and 230 metric tons/day (250 tons/day) of bleached hardwood market pulp. The bleaching sequence is D/COD.

Principal components of the waste treatment system include a primary clarifier, an oxygen-activated sludge treatment facility, and two secondary clarifiers, as indicated in Fig. 6. The center feed peripheral overflow primary clarifier is 38 m (125 ft) in diameter with a side water depth of 3 m (10 ft). It was designed for 55% removal of total suspended solids at a maximum flow of 61,700 m^3/day (16.3 M gpd). In the cooling tower, the temperature of the primary clarifier effluent is reduced to 35°C (95°F). The oxygen-activated sludge basin is 30 m (100 ft) wide by 60 m (200 ft) long with a liquid depth of 3.2 m (10.5 ft) and a gas space of 1.4 m (4.5 ft). Effluent from the oxygen-activated sludge system flows into two peripheral-feed peripheral-overflow secondary clarifiers which are 41 m (135 ft) in diameter with a side water depth of 4.3 m (14 ft). Calculated hydraulic detention times of the primary clarifier, the oxygen-activated sludge basin, and the secondary clarifiers, are 1 hr 50 min, 3 hr 10 min, and 6 hr, respectively.

The oxygen-activated sludge basin mixed liquor volatile suspended solids concentration is controlled to maintain a food to microorganism ratio of 0.7-1.0 day^{-1}. In the first stage of the oxygen-activated sludge basin the pH is controlled between 6.2 and 7.5. The activated sludge recycle ratio is approximately 35%.

During the period of this study, the waste water treatment plant had the following average operating characteristics: Solids Production, 0.43 kg (lb) suspended solids produced/kg (lb) BOD removed; Oxygen Usage, 1.36 kg (lb) O_2 applied/kg (lb) BOD removed; Oxygen Utilization, 94.2%.

For this investigation, samples were taken at the points shown in Fig. 6. The period of composite was eight hours, and four grab samples were taken at each point during that period. Sampling periods were scheduled to account for the detention times of the components of the waste treatment system.

TABLE 9. MILL NO. 3 DATA

Mill No. 3; Location: South; Process: bleached kraft; Bleach Sequence: CEHD

Wood Species: hardwood or softwood

Waste Treatment System: ultrafiltration

	Raw caustic extract	Permeate
Sampling date	7-12*	7-12
BOD, ppm	457	111
Flow rate, m^3/min (gpm)	0.12 (33)	0.0007 (0.19)
Production, metric tons/day (short tons/day)	-- (--)	-- (--)
pH	9.5-10.5	--
Temperature, °C (°F)	46.0 (115)	-- --
Bleach plant products, ppm		
Trichloroguaiacol	1.06	0.204
Tetrachloroguaiacol	0.696	0.128
Epoxystearic acid	6.87	1.58
Dichlorostearic acid	3.17	0.228
Monochloro-dehydroabietic acid	0.356	0.092
Dichloro-dehydroabietic acid	1.24	0.180
Total	13.4	2.4
Chloroform, ppm	0.126	0.101

*Samples were taken on second day of operation. Background data were available only for the first day of operation. Some parameters could be as much as double the numbers indicated, due to recycling of concentrate back to the feed tank.

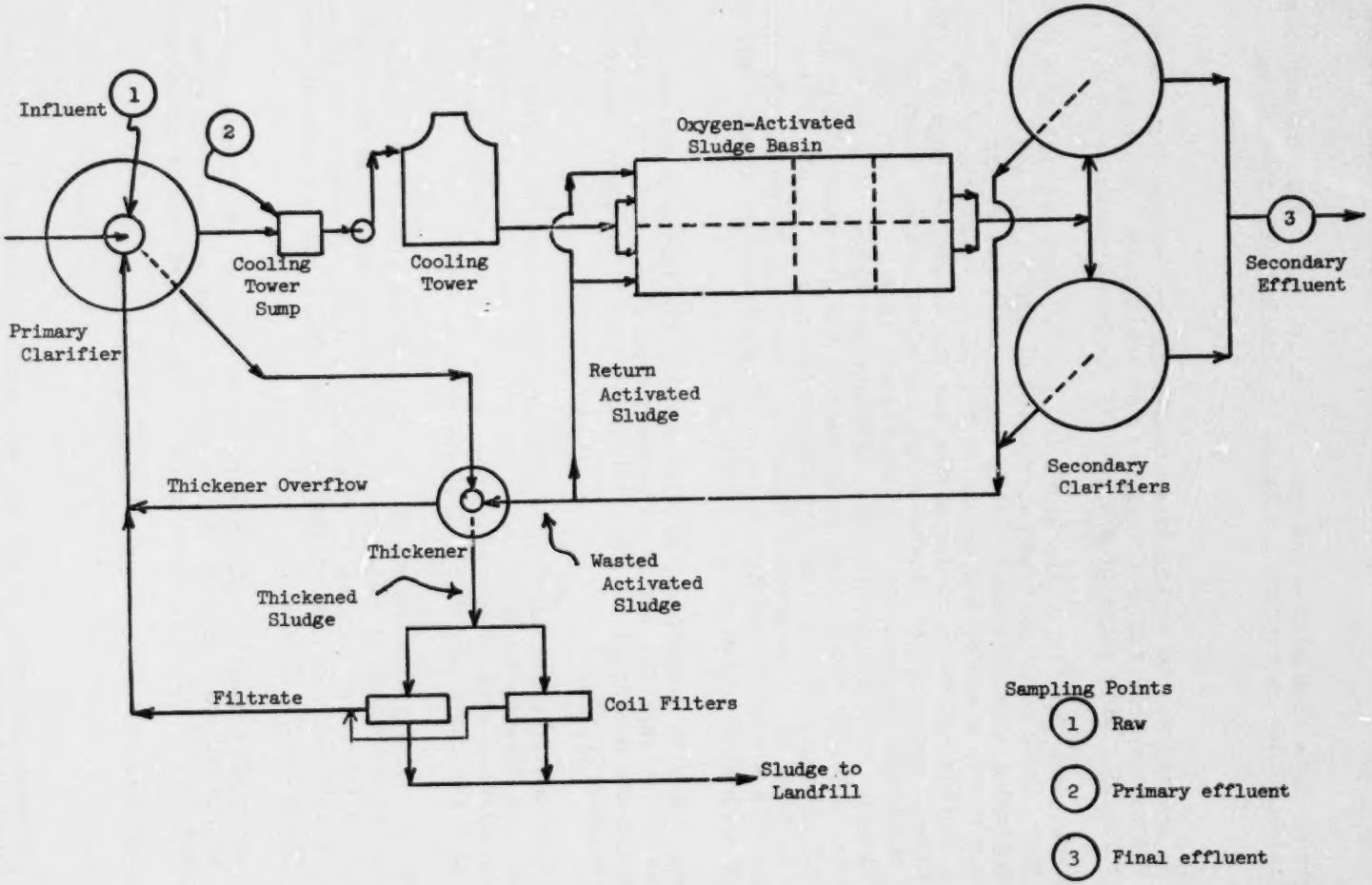


Figure 6. Mill No. 4 waste treatment system.

Thus, the same portion of effluent was sampled as it passed through the facility.

Analytical data from Mill 4 are shown in Table 10. Daily loadings for bleached toxicants and chloroform are based on bleached pulp production.

MILL 5

Mill 5, located in the south, is a totally unbleached operation producing about 408 metric tons/day (450 tons/day) of kraft pulp. The mill pulps principally loblolly pine chips plus about 15% hardwood, which is mostly gum.

Waste treatment facilities are shown in Fig. 7. They consist of a primary clarifier, three parallel oxygen-activated sludge units, and a tertiary clarifier employing alum treatment. Each oxygen-activated sludge unit is 33.4 m (109.5 ft) in diameter and 4.9 m (16 ft) tall. Roughly half the tank volume is a 4-stage activated sludge system and the other half is a clarifier. Effluent, oxygen, and recycled biomass enter the first stage. About 3.7 m (12 ft) of the height is occupied by mixed liquor, leaving 1.2 m (4 ft) of space for oxygen. From the first stage, effluent and oxygen flow to the second and so on to the fourth, and from there to the secondary clarifier. Under current operation the average throughput per unit is 10,670 m^3/day (2.82 M gpd), which gives an average detention time of 3.72 hours. The system operates with a food/microorganism ratio of approximately 1 day^{-1} and a mixed liquor suspended solids of about 2500 ppm.

Effluent flows to a reactor-clarifier forming the tertiary system. Alum mud is added in the tertiary system to bring the pH to 5.0-5.3. This precipitates organics and suspended solids. Effluent from the tertiary clarifier flows to a holding lagoon.

Settled solids from the tertiary clarifier, the primary clarifier, and waste biomass are dewatered and burned. Furnace ash is conveyed to reactor tanks, where sulfuric acid is added to convert the aluminum oxide content of the ash to alum for reuse in the tertiary clarifier.

Because the tertiary system was not running at the time of this study, its operation was simulated by bench-scale alum treatments. Alum was added with stirring to two-liter samples of secondary effluent to reduce the pH to 5. One ppm of cationic polyelectrolyte was also added, and the samples were allowed to settle for 2-2.5 hours.

Time-intervaled composite samples were taken from the mill waste treatment system at the points indicated on the sketch. The samples were taken every 30 minutes for 24 hours and were accumulated in iced sample containers.

Analytical data for these samples are shown in Table 11.

MILL 6

Mill 6 produces unbleached kraft and semichemical pulp and is located in the south. Kraft pulp production, 800-1200 metric tons/day (900-1300 tons/

TABLE 10. MILL NO. 4 DATA

Mill No. 4; Location: East; Process: bleached kraft; Bleach Sequence: D/C OD

Wood Species: pine and various hardwoods

Waste Treatment System: oxygen-activated sludge

	Primary influent			Primary effluent			Final effluent		
Sampling date	4-18	6-6	6-21	4-18	6-6	6-21	4-18	6-6	6-21
BOD, ppm	765	468	489	608	413	482	109	34	38
Flow rate, m^3/min	29.2	33.8	29.9	29.2	33.8	29.9	29.2	33.8	29.9
(gpm)	(7708)	(8930)	(7896)	(7708)	(8930)	(7896)	(7708)	(8930)	(7896)
Production, metric tons/day total	1075	1051	963	1075	1051	963	1075	1051	963
(short tons/day total)	(1185)	(1159)	(1061)	(1185)	(1159)	(1061)	(1185)	(1159)	(1061)
metric tons/day bleached	198	222	352	198	222	352	198	222	352
(short tons/day bleached)	(218)	(245)	(388)	(218)	(245)	(388)	(218)	(245)	(388)
pH	7.4	7.5	6.4	6.9	7.1	6.8	6.7	6.9	6.7
Temperature, °C	54.4	54.4	54.4	51.7	51.7	51.7	35.0	35.0	35.0
(°F)	(130)	(130)	(130)	(125)	(125)	(125)	(95)	(95)	(95)
Fatty and resin acids, ppm									
Oleic	5.30	4.13	3.55	5.29	4.10	4.53	2.34	1.49	1.23
Linoleic	5.58	3.75	3.44	5.19	3.79	4.57	0.43	0.50	0.39
Linolenic	0.25	0.20	0.18	0.26	0.20	0.23	<0.02	0.03	0.02
Pimaric	1.44	1.09	1.37	1.42	1.19	1.83	0.47	0.75	0.89
Isopimaric	2.00	1.38	2.44	1.78	1.63	3.44	0.56	0.86	1.42
Abietic	7.87	5.69	7.49	6.93	6.47	9.97	2.38	2.71	3.63
Dehydroabietic	6.83	5.24	5.08	6.09	5.54	5.78	1.52	1.93	1.93
Total	29.3	21.5	23.6	27.0	22.9	30.4	7.7	8.3	9.5
Daily loading									
kg/day	1229	1046	1013	1134	1116	1307	324	403	410
(lb/day)	(2710)	(2306)	(2236)	(2500)	(2461)	(2881)	(714)	(888)	(903)
kg/ton	1.14	1.00	1.05	1.05	1.06	1.35	0.30	0.38	0.42
(lb/ton)	(2.29)	(1.99)	(2.11)	(2.11)	(2.12)	(2.72)	(0.60)	(0.77)	(0.85)

(Continued)

TABLE 10. (Continued)

Sampling date	Primary influent			Primary effluent			Final effluent		
	4-18	6-6	6-21	4-18	6-6	6-21	4-18	6-6	6-21
Bleach plant products, ppm									
Trichloroguaiacol	0.100	<0.040	0.052	0.136	<0.040	0.044	0.072	<0.040	0.048
Tetrachloroguaiacol	0.052	<0.040	<0.040	0.056	<0.040	<0.040	<0.040	<0.040	<0.040
Epoxystearic acid	0.040	0.236	0.272	<0.040	0.044	0.236	<0.040	<0.040	<0.040
Dichlorostearic acid	0.704	0.312	0.336	0.508	0.220	0.324	0.140	0.156	0.232
Monochloro-dehydroabietic acid	0.412	0.072	0.092	0.400	0.048	0.064	0.236	<0.040	<0.040
Dichloro-dehydroabietic acid	0.140	0.240	0.088	0.124	0.044	0.072	0.068	0.048	0.060
Total	1.41	0.86	0.84	1.22	0.36	0.74	0.52	0.20	0.34
Daily loading									
kg/day	59.3	41.9	36.2	51.3	17.6	31.8	21.9	9.8	14.6
(lb/day)	(131)	(92.3)	(79.7)	(113)	(38.7)	(70.2)	(48.2)	(21.5)	(32.3)
kg/ton	0.30	0.19	0.10	0.26	0.08	0.09	0.11	0.04	0.04
(lb/ton)	(0.60)	(0.38)	(0.20)	(0.52)	(0.16)	(0.18)	(0.22)	(0.09)	(0.08)
Chloroform, ppm	0.571	0.292	0.432	0.394	0.334	0.370	0.051	0.037	0.062
Daily loading									
kg/day	24.0	14.2	18.6	16.6	16.3	15.9	2.14	1.80	2.67
(lb/day)	(52.9)	(31.4)	(41.0)	(36.5)	(35.9)	(35.1)	(4.73)	(3.97)	(5.89)
kg/ton	0.12	0.06	0.05	0.08	0.07	0.04	0.01	0.008	0.008
(lb/ton)	(0.24)	(0.13)	(0.10)	(0.17)	(0.15)	(0.09)	(0.02)	(0.02)	(0.02)

Note: Bleached tonnage is 93-94% hardwoods. Unbleached is softwood.

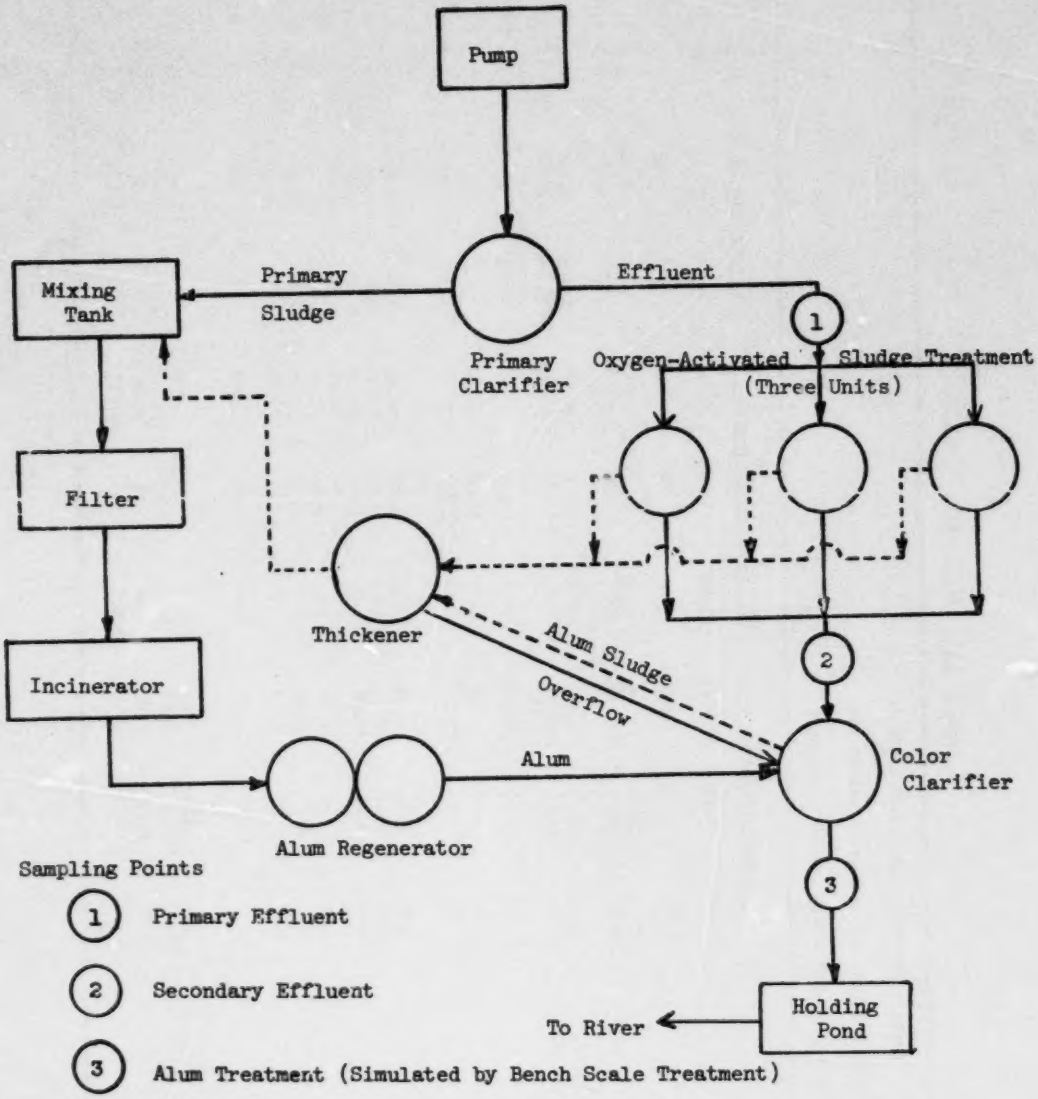


Figure 7. Mill No. 5 waste treatment system.

TABLE 11. MILL NO. 5 DATA

Mill No. 5; Location: South; Process: unbleached kraft

Wood Species: 85% loblolly pine; 15% hardwood — mostly gum

Waste Treatment: oxygen activated sludge and alum treatment

	Primary effluent			Secondary effluent			Alum treated (bench)			Secondary plus polymer
Sampling date	4-20	5-17	6-28	4-20	5-17	6-28	4-20	5-17	6-28	6-28
BOD, ppm	300	325	(90)	30	40	20	8	15	(<1)	--
Flow rate, m^3/min (gpm)	27.3 (7208)	29.6 (7812)	26.9 (7111)	27.3 (7208)	29.6 (7812)	26.9 (7111)	27.3 (7208)	29.6 (7812)	26.9 (7111)	-- --
Production, metric tons/day (short tons/day)	498.1 (549.1)	511.8 (564.2)	542.0 (597.4)	498.1 (549.1)	511.8 (564.2)	542.0 (597.4)	498.1 (549.1)	511.8 (564.2)	542.0 (597.4)	542.0 (597.4)
pH	7.4-8.1	8.7-9.3	8.5-9.7	6.4	6.3-6.4	7.3	--	--	--	--
Temperature, °C (°F)	32-33 (89-91)	35-36 (95-97)	37-38 (99-100)	32-33 (89-91)	35-36 (95-97)	37-38 (99-100)	-- (--)	-- (--)	-- (--)	-- (--)
Fatty and resin acids, ppm										
Oleic	1.93	2.49	0.53	0.36	1.08	<0.02	<0.02	<0.02	<0.02	<0.02
Linoleic	0.98	1.16	0.12	0.14	0.08	<0.02	<0.02	<0.02	<0.02	<0.02
Linolenic	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pimaric	0.54	0.81	0.41	0.28	0.52	0.06	<0.02	<0.02	<0.02	0.03
Isopimaric	0.46	0.75	0.44	0.21	0.48	<0.02	<0.02	<0.02	<0.02	<0.02
Abietic	1.61	2.27	1.49	0.77	0.52	0.08	<0.02	<0.02	<0.02	0.04
Dehydroabietic	1.79	3.46	2.45	0.41	0.46	0.06	<0.02	<0.02	<0.02	0.04
Total	7.31	10.90	5.44	2.07	3.14	0.20	--	--	--	0.11
Daily loading										
kg/day (lb/day)	287 (634)	464 (1024)	211 (465)	81.8 (179)	134 (295)	7.8 (17.1)	-- (--)	-- (--)	-- (--)	4.3 (9.4)
kg/ton pulp (lb/ton pulp)	0.58 (1.15)	0.90 (1.81)	0.39 (0.78)	0.16 (0.32)	0.26 (0.52)	0.01 (0.03)	-- (--)	-- (--)	-- (--)	0.01 (0.02)

day), employs Kamyr digesters with internal "Hi-Heat" washing followed by two conventional cylinder washers; the wood is loblolly pine. Hardwoods (10-20% gum, the rest primarily oak) are pulped by a continuous green liquor semi-chemical process (17-20 minutes at 180°C). Production is about 180 metric tons/day (200 tons/day). The corrugating medium paper machine white water system is closed, so that spent liquors are normally lost only from pulping and washing leaks, spills, vacuum pump carry-over, and felt washing. Included in the discharge from semichemical pulping is wood sap squeezed out at the digester feed screws, 0.06-0.07 m^3/min (15-20 gpm) at 16,000 ppm BOD.

Of principal interest in this project is the mill's lime treatment color removal system. Lime slurry is prepared at about 10% consistency and added to raw waste at about 1000 ppm lime based on weight of effluent. As indicated in Fig. 8, the treated waste passes into the color clarifier, which is 41 m (135 ft) in diameter. At a maximum rise rate of 58.7 m^3/m^2-day (1440 gal/day-ft^2), this provides a capacity of 68,130 m^3/day (18 M gpd). From the color clarifier, effluent passes to a 9 m (30 ft) diameter by 3.6 m (12 ft) deep carbonation tank where lime kiln stack gas is introduced. Calcium carbonate formed by carbon dioxide reaction with the remaining calcium hydroxide is settled in a second clarifier, called the carbonation clarifier, which is essentially identical with the color clarifier. Sludge from the color clarifier is dewatered and sent to the lime kiln. Effluent from the color removal process enters a lagoon system; study of the lagoon system is not included in this project.

Sampling periods for this study were of eight hours duration. A flow-proportional sampler was used for raw waste, and continuous, peristaltic pump samplers were used for the other two stages. The sampling periods were offset for the estimated holdup time in the clarifiers. Sample receivers were cooled in an ice bath. The process in this mill is sufficiently variable to make samples taken only a few days apart represent a typical range of mill operations. Consequently, intervals between the three samplings were shorter than for most mills in this project. During the second and third samplings, recarbonation and final clarification for the sampling were accomplished on a pilot scale sidestream to avoid interference of solids carryover from the color clarifier. The only deviation from normal process conditions should have been a lower temperature, which could affect retention of soluble or condensible gases from the kiln.

Analytical data for this mill are shown in Table 12.

MILL 7

Mill 7, located in the east, uses the sulfite process and produces bleached pulp from mixed eastern hardwoods. Separate systems are used to treat the pulp mill waste, which has high oxygen demand, and the paper mill waste containing significant amounts of suspended solids. Only the pulp mill waste control facility is of interest in this project. Spent liquors collected from the multistage countercurrent brownstock washers are evaporated and burned without chemical recovery. Volatile organic material in evaporator distillate, dilute spent liquors from the prebleach washers, and spent

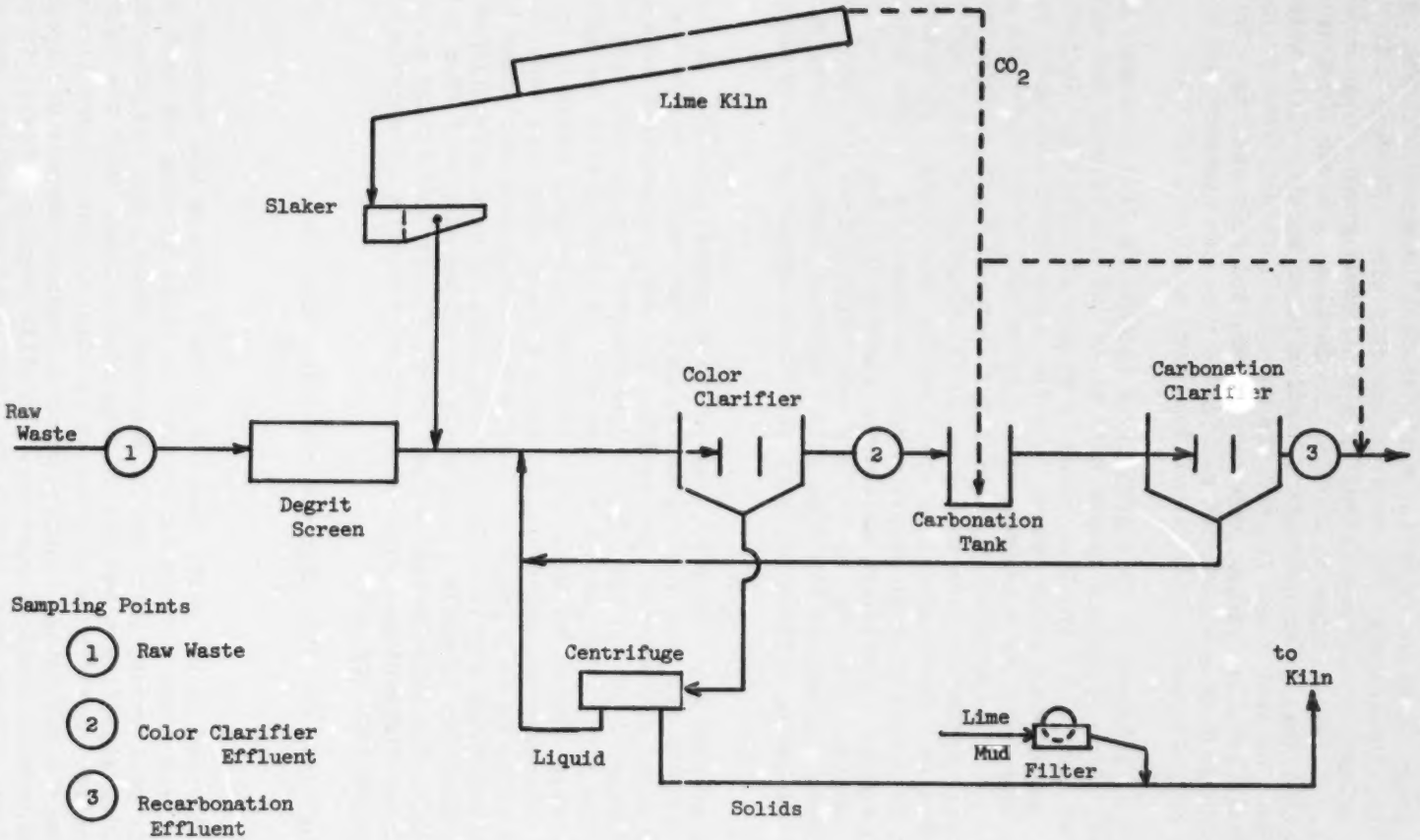


Figure 8. Mill No. 6 color removal process.

TABLE 12. MILL NO. 6 DATA

Mill No. 6; Location: South; Process: unbleached kraft and semichemical

Wood species: loblolly pine (kraft); 10-20% gum, oak (semichemical)

Waste treatment: lime color removal and recarbonation

	Raw			Color clarifier effluent			Recarbonation effluent		
Sampling date	6-16	6-23	6-27	6-16	6-23	6-27	6-16	6-23	6-27
BOD, ppm	134	338	267	103	205	186	101	212	190
Flow rate, m^3/min	32	30.5	27.5	32	30.5	27.5	32	30.5	27.5
(gpm)	(8453)	(8062)	(7263)	(8453)	(8062)	(7263)	(8453)	(8062)	(7263)
Production, metric tons total	948	992	1386	948	992	1386	948	992	1386
(short tons total)	(1045)	(1093)	(1528)	(1045)	(1093)	(1528)	(1045)	(1093)	(1528)
metric tons, kraft	948	816	1202	948	816	1202	948	816	1202
(short tons kraft)	(1045)	(899)	(1325)	(1045)	(899)	(1325)	(1045)	(899)	(1325)
pH	9.5	9.3	8.4	12.0	12.0	12.0	10.3	10.6	10.6
Temperature, °C	44.0	45.0	45.0	--	--	--	--	--	--
(°F)	(111)	(113)	(113)	(--)	(--)	(--)	(--)	(--)	(--)
Fatty and resin acids, ppm									
Oleic	6.62	9.26	11.32	0.66	1.09	0.82	0.22	0.43	0.09
Linoleic	5.06	7.97	9.25	0.46	1.02	0.43	0.24	0.66	0.22
Linolenic	0.12	0.21	0.24	0.02	0.03	0.02	<0.02	<0.02	<0.02
Pimaric	0.90	1.54	1.58	0.37	0.38	0.30	0.38	0.33	0.30
Isopimaric	1.16	2.15	1.91	0.44	0.41	0.36	0.45	0.48	0.35
Abietic	3.46	7.04	6.65	1.68	2.28	1.96	1.76	2.25	1.82
Dehydroabietic	3.33	6.30	6.08	2.80	3.95	3.61	2.99	4.07	3.80
Total	20.6	34.5	37.0	6.4	9.2	7.5	6.0	8.2	6.6
Daily loading									
kg/day	949	1517	1466	295	405	297	277	361	261
(lb/day)	(2093)	(3344)	(3232)	(650)	(892)	(655)	(610)	(795)	(576)
kg/ton pulp	1.0	1.5	1.1	0.31	0.41	0.21	0.29	0.36	0.19
(lb/ton pulp)	(2.0)	(3.1)	(2.1)	(0.62)	(0.82)	(0.43)	(0.58)	(0.73)	(0.38)

bleach wash waters are neutralized in pH and subjected to biological degradation in an activated sludge plant.

As shown in Fig. 9, variations in waste strength and flow are equalized in a basin which has an effective detention time of 2.5 hours. The waste is then aerated for a theoretical detention time of 24 hours. Aeration is achieved with mechanical surface aerators. The food to microorganism ratio for an average mixed liquor volatile suspended solids of 6000 ppm is about 0.7 day^{-1}. Sludge production is 0.5 kg (lb) mixed liquor total suspended solids per kg (lb) BOD removed. Prior to release to the river, the effluent passes through a clarifier which has a theoretical detention time of 6 hours.

Samples analyzed in this project were composites of one-hour grab samples collected over 24 hours. The samples were not proportional to flow since the normal flow variation is only about $\pm$ 10%.

Analytical data for Mill 7 are shown in Table 13. In the table, Influent A and B and Effluent A and B refer to duplicate samples collected on the dates indicated.

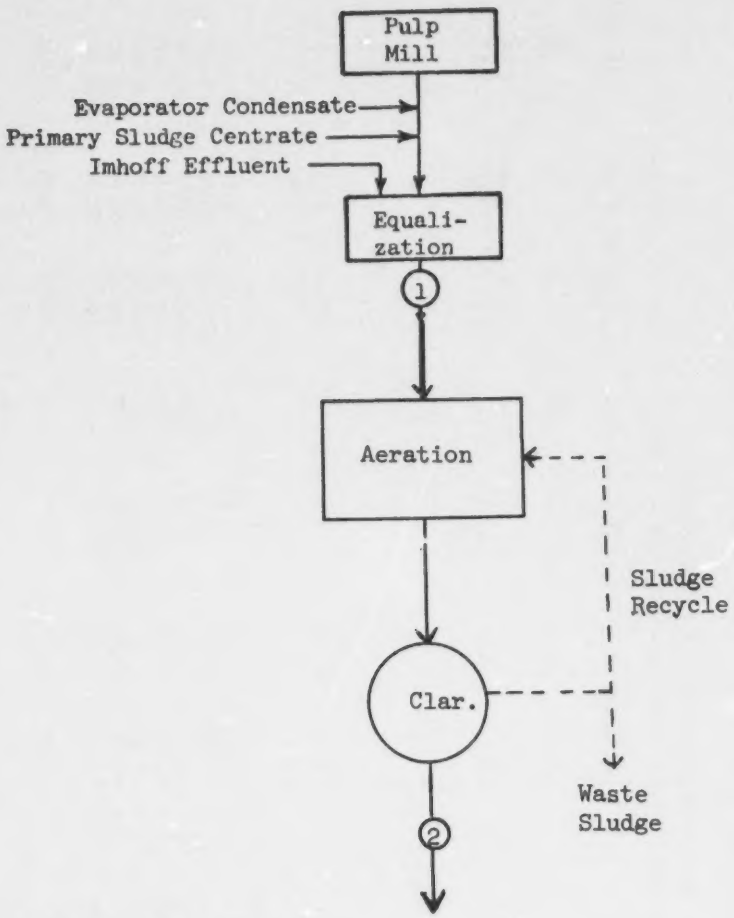
MILL 8

Mill 8, located on the west coast, produces about 875 metric tons/day (900 tons/day) of bleached kraft pulp from sawdust and western hemlock. Its bleaching sequence is CEHED. The mill also produces 249-272 metric tons/day (275-300 tons/day) of refiner groundwood.

Principal features of the mill's waste treatment facility include a primary clarifier of 76.2 m (250 ft) diameter and an activated sludge system. The bleach sewer bypasses the primary clarifier and goes directly to secondary treatment, as indicated in Fig. 10. Also shown in the figure is the wasting of secondary sludge back to the primary clarifier. This sludge wasting occurs at a flow rate of 1.9 m^3/min (500 gpm) for eight hours per day. Nominal flows for the principal streams into the waste treatment system are bleach sewer 57,000 m^3/day (15 $\overline{M}$ gpd) and process sewer 95,000 m^3/day (25 $\overline{M}$ gpd). Consequently, the flow of wasted sludge contributes only slightly to total effluent flow from the primary clarifier. The primary clarifier, holding pond, and aeration basin each have detention times of 8 hours. Detention time in the secondary clarifiers is 6 hours. The activated sludge system operates with a food/microorganism ratio of 0.12 day^{-1}, a mixed liquor suspended solids of 5983 ppm, and a sludge volume index of 99.5 ml/g. Diameter of the secondary clarifier is 64 m (210 ft).

Samples for this investigation were taken at the points shown in Fig. 10. Grab samples from the process sewer, the bleach sewer, and the primary clarifier effluent were taken each hour for nine hours. Secondary effluent to the river was sampled automatically with a refrigerated sampler.

Analytical data for these samples are shown in Table 14.



Sampling Points

(1) Activated Sludge Influent

(2) Activated Sludge Effluent

Figure 9. Mill No. 7 waste treatment system.

TABLE 13. MILL NO. 7 DATA

Mill No. 7; Location: East; Process: bleached sulfite; Bleach Sequence: hypochlorite

Wood Species: mixed eastern hardwoods

Waste Treatment System: activated sludge — no primary clarifier

	Influent A		Influent B		Effluent A		Effluent B	
Sampling date	5-16	5-24	5-16	5-24	5-16	5-24	5-16	5-24
BOD, ppm	1660	1930	1660	1930	67	--	67	--
Flow rate, m^3/min (gpm)	7.28 (1924)	7.44 (1965)	7.28 (1924)	7.44 (1965)	7.28 (1924)	7.44 (1965)	7.28 (1924)	7.44 (1965)
Production, metric tons/day	--	--	--	--	--	--	--	--
(short tons/day)	--	--	--	--	--	--	--	--
pH	--	--	--	--	6.8	6.8	6.8	6.8
Temperature, °C	--	--	--	--	29.4	32.2	29.4	32.2
(°F)	--	--	--	--	(85)	(90)	(85)	(90)
Fatty and resin acids, ppm*								
Oleic	0.95	0.30	1.04	0.32	0.37	0.24	0.34	0.21
Linoleic	0.98	0.61	1.11	0.66	<0.02	<0.02	<0.02	<0.02
Linolenic	0.30	0.17	0.39	0.18	<0.02	<0.02	<0.02	<0.02
Pimaric	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Isopimaric	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Abietic	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Dehydroabietic	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Total	2.23	1.08	2.54	1.16	0.37	0.24	0.34	0.21
Daily loading								
kg/day	23.4	11.6	26.6	12.4	3.9	2.6	3.6	2.2
(lb/day)	(51.6)	(25.5)	(58.7)	(27.4)	(8.6)	(5.7)	(7.9)	(5.0)
kg/ton	--	--	--	--	--	--	--	--
(lb/ton)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)

(Continued)

TABLE 13. (Continued)

Sampling date	Influent A 5-16	Influent A 5-24	Influent B 5-16	Influent B 5-24	Effluent A 5-16	Effluent A 5-24	Effluent B 5-16	Effluent B 5-24
Bleach plant products, ppm *								
Trichloroguaiacol	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Tetrachloroguaiacol	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Epoxystearic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichlorostearic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Monochloro-dehydroabietic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichloro-dehydroabietic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Total	--	--	--	--	--	--	--	--
Daily loading								
kg/day	--	--	--	--	--	--	--	--
(lb/day)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)
kg/ton	--	--	--	--	--	--	--	--
(lb/ton)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)
Chloroform, ppm	1.374	1.194	1.364	1.292	0.052	0.028	0.049	0.031
Daily loading								
kg/day	14.4	12.8	14.3	13.8	0.54	0.30	0.51	0.33
(lb/day)	(31.8)	(28.2)	(31.5)	(30.5)	(1.2)	(0.66)	(1.13)	(0.73)
kg/ton	--	--	--	--	--	--	--	--
(lb/ton)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)

*Method modification necessary for these samples. The samples were adjusted to pH 5 instead of 3 prior to the ether extraction. The combined extracts were washed three times with distilled water (25 cm^3).

TABLE 13. (Continued)

Sampling date	Influent A		Influent B		Effluent A		Effluent B	
	5-16	5-24	5-16	5-24	5-16	5-24	5-16	5-24
Bleach plant products, ppm *								
Trichloroguaiacol	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Tetrachloroguaiacol	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Epoxystearic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichlorostearic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Monochloro-dehydroabietic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichloro-dehydroabietic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Total	--	--	--	--	--	--	--	--
Daily loading								
kg/day	--	--	--	--	--	--	--	--
(lb/day)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)
kg/ton	--	--	--	--	--	--	--	--
(lb/ton)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)
Chloroform, ppm	1.374	1.194	1.364	1.292	0.052	0.028	0.049	0.031
Daily loading								
kg/day	14.4	12.8	14.3	13.8	0.54	0.30	0.51	0.33
(lb/day)	(31.8)	(28.2)	(31.5)	(30.5)	(1.2)	(0.66)	(1.13)	(0.73)
kg/ton	--	--	--	--	--	--	--	--
(lb/ton)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)

*Method modification necessary for these samples.
The samples were adjusted to pH 5 instead of 3 prior to the ether extraction. The combined extracts were washed three times with distilled water (25 cm^3).

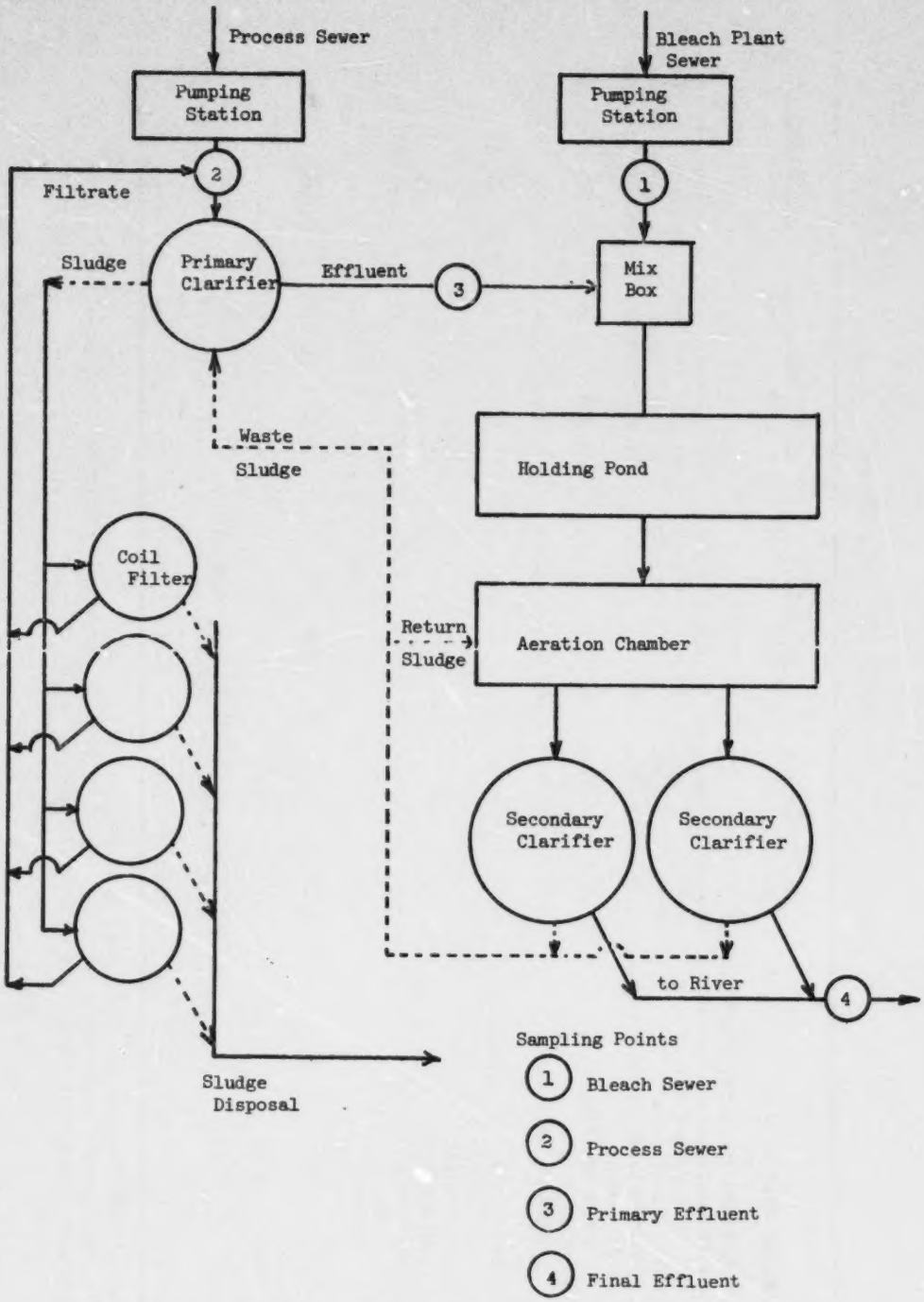


Figure 10. Mill No. 8 waste treatment system.

TABLE 14. MILL NO. 8 DATA

Mill No. 8; Location: West Coast; Process: bleached kraft and refiner groundwood; Bleach Sequence: CEHED

Wood Species: hemlock, sawdust

Waste Treatment System: primary clarifier and activated sludge

	Process effluent			Primary effluent			Final effluent		
Sampling date	4-19	5-2	5-17	4-19	5-2	5-17	4-19	5-2	5-19
BOD, ppm	--	300	250	--	310	306	--	12	16
Flow rate, m^3/min (gpm)	65.7 (17360)	69.6 (18400)	70.4 (18610)	65.7 (17360)	69.6 (18400)	70.4 (18610)	97.2 (25690)	105 (27780)	110 (29170)
Production, metric tons/day brownstock (short tons/day) brownstock	750.2 (826.9)	861.0 (949.7)	861.0 (949.7)	750.2 (826.9)	861.0 (949.7)	861.0 (949.7)	750.2 (826.9)	861.0 (949.7)	861.0 (949.7)
pH	10.2	10.1	10.4	9.6	9.8	9.5	7.9	7.7	7.4
Temperature, °C (°F)	32.2 (90.0)	32.2 (90.0)	35.0 (95.0)	30.0 (86.0)	32.2 (90.0)	32.8 (91.0)	26.1 (79.0)	26.1 (79.0)	25.6 (78.0)
Fatty and resin acids, ppm									
Oleic	1.93	0.87	1.06	1.21	1.30	2.05	0.12	<0.02	0.17
Linoleic	1.75	0.70	0.56	0.61	0.46	1.02	<0.02	0.11	0.05
Linolenic	0.21	0.06	<0.02	0.15	<0.02	<0.02	<0.02	<0.02	<0.02
Pimaric	0.10	0.25	0.07	0.13	0.17	0.13	<0.02	<0.02	<0.02
Isopimaric	1.42	2.99	2.66	1.35	3.55	4.80	<0.02	<0.02	0.05
Abietic	1.47	2.21	1.62	1.30	3.29	3.46	<0.02	<0.02	<0.02
Dehydroabietic	1.58	2.98	3.30	1.49	3.53	4.58	<0.02	<0.02	<0.02
Total	8.5	10.1	9.3	6.2	11.3	16.0	0.12	0.11	0.27
Daily loading									
kg/day (lb/day)	803 (1770)	1014 (2235)	941 (2074)	590 (1300)	1134 (2500)	1629 (3590)	16.8 (37)	16.8 (37)	43.1 (95)
kg/ton (lb/ton)	1.1 (2.1)	1.2 (2.4)	1.1 (2.2)	0.8 (1.6)	1.3 (2.6)	1.9 (3.8)	0.022 (0.045)	0.020 (0.039)	0.050 (0.100)

(Continued)

TABLE 14. (Continued)

	Bleach sewer effluent			Final effluent		
Sampling date	4-19	5-2	5-17	4-19	5-2	5-19
Bleach plant products, ppm						
Trichloroguaiacol	0.044	<0.040	<0.040	<0.040	<0.040	<0.040
Tetrachloroguaiacol	0.060	<0.040	<0.040	<0.040	<0.040	<0.040
Epoxystearic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichlorostearic acid	<0.040	0.080	0.084	<0.040	<0.040	<0.040
Monochloro-dehydroabietic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichloro-dehydroabietic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Total	0.10	0.080	0.084	--	--	--
Daily loading						
kg/day	4.54[1]	4.08[1]	4.85[1]	--	--	--
(lb/day)	(10.0)	(9.0)	(10.7)	(--)	(--)	(--)
kg/ton	0.0069[1]	0.0050[1]	0.0055[1]	--	--	--
(lb/ton)	(0.014)	(0.010)	(0.011)	(--)	(--)	(--)
Chloroform, ppm	4.582	3.064	5.369	0.021	0.077	0.075
Daily loading						
kg/day	208[1]	156[1]	309[1]	2.94[2]	11.7[2]	11.9[2]
(lb/day)	(459)	(345)	(681)	(6.49)	(25.7)	(26.3)
kg/ton	0.316[1]	0.192[1]	0.350[1]	0.0045[2]	0.0140[2]	0.0135[2]
(lb/ton)	(0.63)	(0.385)	(0.701)	(0.0089)	(0.0286)	(0.0271)
Production, metric tons/day bleached	659.5	814.7	881.8	659.5	814.7	659.5
(short tons/day) bleached	(727)	(898)	(972)	(727)	(898)	(727)

Note: Bleach plant effluent by-passes primary clarifier.

[1] Based on bleach plant production and bleach plant flow.

[2] Based on bleach plant production and total plant flow.

MILL 9

Mill 9, located in the south, produces about 1360 metric tons (1500 tons) of paperboard per day. Typical pulp production includes about 1225 metric tons/day (1350 tons/day) unbleached pine kraft, of which up to 181 metric tons/day (200 tons/day) are subsequently bleached, and about 91 metric tons/day (100 tons/day) of hardwood semichemical. Because bleached pulp production is small compared with total production, this is considered to be an unbleached mill for the purpose of this project.

As indicated in Fig. 11, the mill's waste treatment facilities consist of a primary clarifier and a 25.5 ha (63 acre) aerated lagoon. Twenty-seven 56-kw (75-hp) aerators are employed in the first two-thirds of the lagoon. Detention times are 5 hours in the clarifier and 10 days in the lagoon. Typical effluent flow is 114,000 m^3/day (30 $\overline{M}$ gpd).

Raw and primary waste samples taken for this study were composites of grab samples collected at two-hour intervals over an eight-hour period. The sampling period for the primary effluent was delayed five hours to account for the detention time of the clarifier. The lagoon outfall was sampled continuously with a timed sampler into a refrigerated container. Lagoon outfall and primary effluent samples were taken during the same period.

Analytical data for Mill 9 are listed in Table 15.

MILL 10

Mill 10 is a west coast, ammonium bisulfite mill which produces bleached pulp. Bleaching sequence is CEH, daily pulp capacity is 281 metric tons (310 tons), and primary wood species is western hemlock.

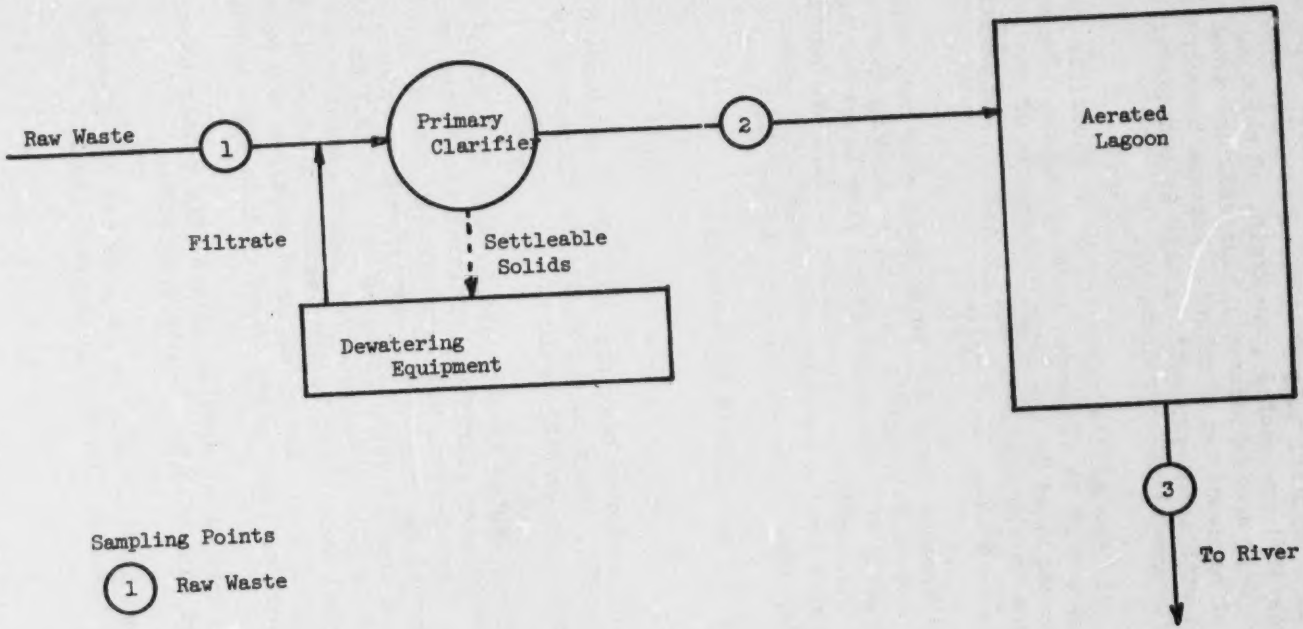
The mill's waste treatment system is sketched in Fig. 12. After leaving the 45.7 m (150 ft) diameter primary clarifier, effluent enters the two-cell aerated lagoon system. The first lagoon, with a detention time of two days and an area of 6.5 ha (16 acres) has eleven 74.6-kw (100-hp) aerators. The second lagoon has a detention time of seven days, an area of 20.7 ha (51 acres), and employs six 74.6-kw (100-hp) aerators. Lagoon capacity is 600,000 m^3 (150 $\overline{M}$ gal). Normal waste load to the lagoons is 13,600-18,150 kg/day (30,000-40,000 lb/day) of BOD. Bleach effluent bypasses the primary clarifier and joins the primary effluent prior to entry into the lagoons.

For this study, samples were taken continuously at the points shown on the sketch, refrigerated, and submitted as 24-hour composites.

Analytical data are shown in Table 16. Daily loadings for bleached toxicants and chloroform are based on bleached pulp production.

MILL 11

Nominal production at this mill amounts to 726 metric tons/day (800 tons/day) of bleached kraft pulp and 118 metric tons/day (130 tons/day) bleached groundwood. The kraft mill production is regularly changed from



Sampling Points

1 Raw Waste

2 Primary Effluent

3 Final Effluent

Figure 11. Mill No. 9 waste treatment system.

TABLE 15. MILL NO. 9 DATA

Mill No. 9; Location: South; Process: unbleached kraft and semichemical

Wood Species: 90-95% pine, 5-10% hardwood

Waste Treatment: primary clarifier and aerated lagoon

	Raw			Primary			Final		
Sampling date	4-18	5-9	5-24	4-18	5-9	5-24	4-18	5-9	5-24
BOD, ppm	395	300	220	387	254	195	58	79	58
Flow rate, m^3/min	78.3	86.2	73.1	78.3	86.2	73.1	78.3	86.2	73.1
(gpm)	(20690)	(22780)	(19306)	(20690)	(22780)	(19306)	(20690)	(22780)	(19306)
Production, metric tons/day	1364	1306	1335*	1364	1306	1335*	1364	1306	1335*
(short tons/day)	(1504)	(1440)	(1472)*	(1504)	(1440)	(1472)*	(1504)	(1440)	(1472)*
pH	8.6	7.7	9.8	8.3	7.7	9.8	7.8	7.4	7.8
Temperature, °C	36-37	39-40	34	35-36	38-39	32	29-30	34-35	30
(°F)	(97-99)	(102-104)	(93)	(95-97)	(100-102)	(90)	(84-86)	(93-95)	(86)
Fatty and resin acids, ppm									
Oleic	3.95	4.65	7.57	5.89	4.55	5.71	0.51	0.82	1.17
Linoleic	2.25	2.96	4.21	3.18	2.83	3.15	0.09	0.17	0.19
Linolenic	0.25	0.09	0.21	0.09	0.02	0.15	<0.02	<0.02	<0.02
Pimaric	1.53	0.96	2.46	1.49	1.14	1.84	1.49	1.95	2.01
Isopimaric	2.38	2.25	4.20	2.31	1.84	3.12	1.20	1.32	1.69
Abietic	5.69	6.45	10.06	4.76	5.30	7.35	2.39	2.28	2.65
Dehydroabietic	6.27	7.83	9.84	5.45	4.50	8.49	1.90	2.27	2.88
Total	22.3	25.2	38.55	23.2	20.2	29.81	7.58	8.81	10.59
Daily loading									
kg/day	2517	3134	4059	2617	2509	3139	857	1094	1115
(lb/day)	(5550)	(6902)	(8949)	(5770)	(5532)	(6920)	(1890)	(2413)	(2458)
kg/ton pulp	1.8	2.4	3.0*	1.9	1.9	2.4*	0.6	0.8	0.8*
(lb/ton pulp)	(3.8)	(4.8)	(6.1)*	(4.0)	(3.8)	(4.7)*	(1.3)	(1.7)	(1.7)*

*Based on average tonnage of 1472 tons.

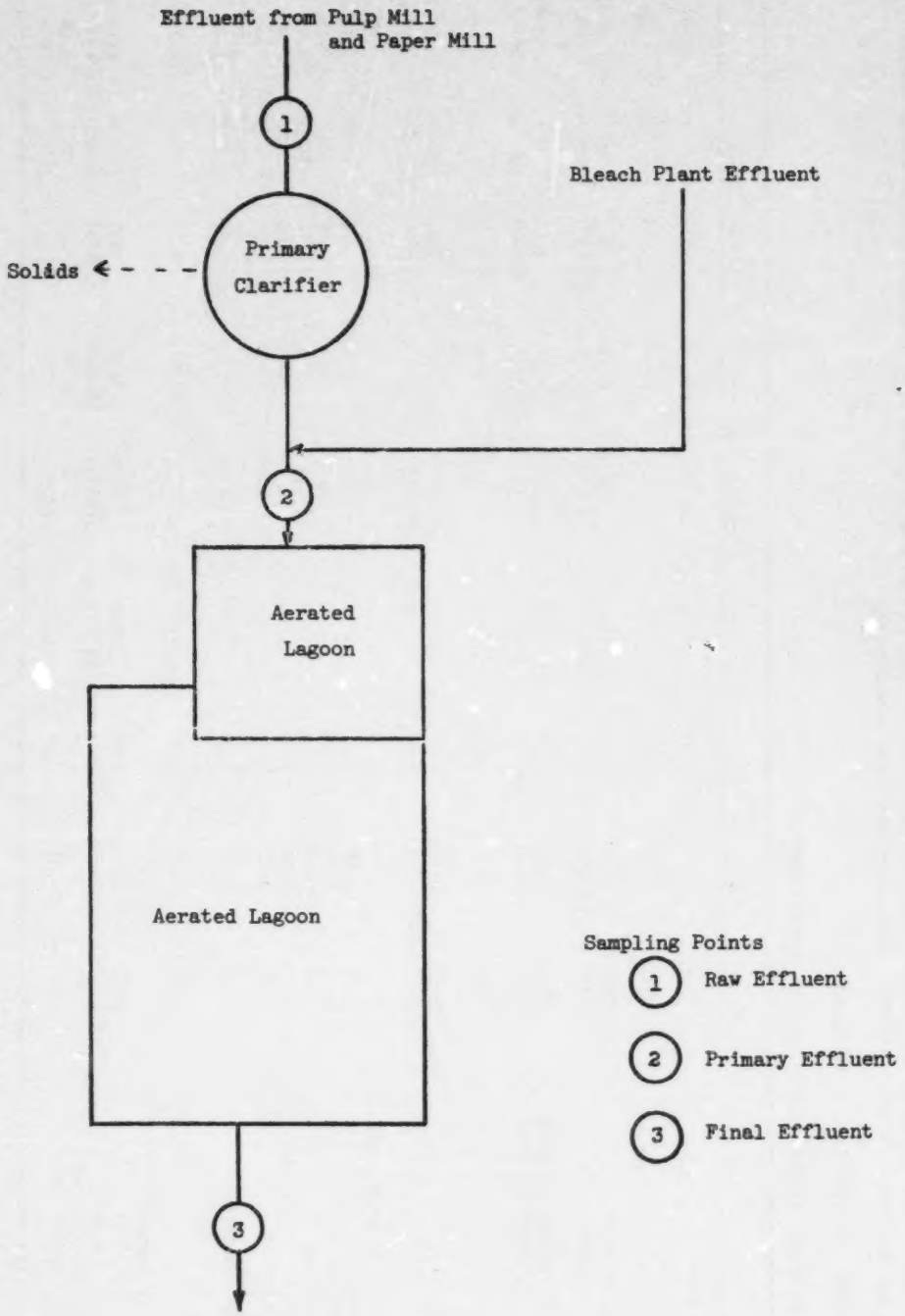


Figure 12. Mill No. 10 waste treatment system.

TABLE 16. MILL NO. 10 DATA

Mill No. 10; Location: West Coast; Process: bleached sulfite; Bleach Sequence: CEH

Wood Species: western hemlock

Waste Treatment System: primary clarifier and lagoon

	Raw			Input to secondary			Secondary		
Sampling date (rec'd)	4-22	4-26	5-16	4-22	4-26	5-16	4-22	4-26	5-16
BOD, ppm	--	--	--	200	150	153	37	30	35
Flow rate, m^3/min	22.3	22.3	22.3	43.8	43.4	42.4	43.8	43.4	42.4
(gpm)	(5903)	(5903)	(5903)	(11580)	(11460)	(11212)	(11580)	(11460)	(11212)
Production, metric tons/day	212	225	216	212	225	216	212	225	216
(short tons/day)	(234)	(248)	(238)	(234)	(248)	(238)	(234)	(248)	(238)
pH	--	--	--	7.1	6.5	8.0	6.9	7.0	7.2
Temperature, °C	--	--	--	--	--	--	18	18	17
(°F)	--	--	--	--	--	--	(64.4)	(64.4)	(62.6)
Fatty and resin acids, ppm									
Oleic	0.20	0.04	0.09	0.14	0.06	0.02	0.12	0.02	0.02
Linoleic	0.12	<0.02	0.06	0.06	<0.02	<0.02	<0.02	<0.02	<0.02
Linolenic	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pimaric	0.06	0.09	0.09	<0.02	0.02	0.03	<0.02	<0.02	<0.02
Isopimaric	0.09	0.06	0.11	<0.02	0.08	0.04	<0.02	<0.02	<0.02
Abietic	0.43	0.13	0.33	0.10	0.06	<0.02	<0.02	<0.02	<0.02
Dehydroabietic	2.94	2.06	2.62	1.72	1.41	1.00	<0.02	<0.02	<0.02
Total	3.84	2.38	3.30	2.02	1.63	1.09	0.12	0.02	0.02
Daily loading									
kg/day	123	76.7	106	127	102	66.7	7.7	1.4	1.2
(lb/day)	(272)	(169)	(234)	(281)	(224)	(147)	(17)	(3)	(2.7)
kg/ton	0.58	0.34	0.49	0.60	0.45	0.31	0.036	0.006	0.006
(lb/ton)	(1.16)	(0.72)	(0.98)	(1.20)	(0.90)	(0.62)	(0.073)	(0.011)	(0.011)

(Continued)

TABLE 16. (Continued)

Sampling date (rec'd)	Raw			Input to secondary			Secondary		
	4-22	4-26	5-16	4-22	4-26	5-16	4-22	4-26	5-16
Bleach plant products, ppm									
Trichloroguaiacol	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Tetrachloroguaiacol	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Epoxystearic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichlorostearic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Monochloro-dehydroabietic acid	0.048	<0.040	<0.040	<0.040	0.048	<0.040	<0.040	<0.040	<0.040
Dichloro-dehydroabietic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Total	0.05	--	--	--	0.05	--	--	--	--
Daily loading									
kg/day	1.61	--	--	--	3.16	--	--	--	--
(lb/day)	(3.55)	(--)	(--)	(--)	(6.96)	(--)	(--)	(--)	(--)
kg/ton	0.0076	--	--	--	0.014	--	--	--	--
(lb/ton)	(0.015)	(--)	(--)	(--)	(0.030)	(--)	(--)	(--)	(--)
Chloroform, ppm	0.019	0.023	0.006	0.127	0.057	0.088	0.008	0.011	0.007
Daily loading									
kg/day	0.61	0.74	0.19	8.0	3.6	5.4	0.50	0.69	0.42
(lb/day)	(1.35)	(1.63)	(0.42)	(17.7)	(7.85)	(11.86)	(1.11)	(1.52)	(0.94)
kg/ton	0.0029	0.0033	0.0009	0.038	0.016	0.025	0.0024	0.0031	0.0020
(lb/ton)	(0.0058)	(0.0066)	(0.0018)	(0.076)	(0.032)	(0.050)	(0.0048)	(0.0061)	(0.0039)

Note: Loads for raw are based on flow of 8-9 $\overline{M}$ gpd.

hardwood pulp to softwood pulp, with the grade change occurring at intervals of approximately 20 to 36 hours. Mill 11 is located in the northern midwest.

The mill's effluent treatment facilities consist principally of primary clarifiers and an aerated lagoon system, as shown in Fig. 13. Two primary clarifiers, arranged in parallel, are 54.9 m and 61 m (180 and 200 ft) in diameter and have 3 hours detention time. The first aerated lagoon is 4.3 m (14 ft) deep, holds 454,000 m^3 (120 M gal), and has five 44.7-kw (60-hp) and two 55.9-kw (75-hp) aerators. The second lagoon has a controllable depth; normally it is 2.4 m (8 ft) deep with a volume of 757,000 m^3 (200 M gal). It employs twelve 44.7-kw (60-hp) aerators. Detention times in the lagoons are 4.0 and 6.7 days. Between the lagoons and the river are an 18.3 m (60 ft) diameter flocculator and an 82.3 m (270 ft) diameter secondary clarifier with 4.5 hours detention time.

An additional component of the mill's environmental control system is a steam stripping column used to reduce odor and BOD in condensates produced in the kraft process. Waste waters collected for steam stripping include hot water accumulator overflows from digester blows, turpentine decanter underflow, evaporator hot-well condensates, water seal tank purge water, and condensates from odorous gas conveyance pipelines. The stripper column is 16 m (53 ft) high, 2.2 m (7.3 ft) in diameter, and consists of a 24-tray column with 46 bubble caps per tray. Feed enters near the top of the fourth plate down in the column and 4.22 kg/cm^2 (60 psi) steam enters at the bottom. Concentrated odorous gases removed at the top of the column go to the lime kiln or incinerator for combustion. Stripper effluent ultimately goes to the mill process sewer.

Samples were taken over 48-hour periods in order to contain effluents from both hardwood and softwood pulp production. There was no attempt made to account for effluent treatment system delays in scheduling the sampling, so effluent samples would tend to favor the pulp being run at the start of sampling. Sample set 1 began with hardwood and ended with softwood; set 2 was the reverse. Set 3 covered two grade changes beginning with a softwood run.

Individual grab samples, approximately proportional to flow, were refrigerated and then blended to produce a composite sample at the end of the sampling period. Sampling points are shown in Fig. 13. Steam stripper influent and effluent samples were also taken.

Analytical data are shown in Table 17. Daily loadings for bleached toxicants and chloroform are based on bleached pulp production.

MILL 12

This mill, located in the east, produces approximately 454 metric tons/day (500 tons/day) of bleached pulp. Separate lines for mixed hardwoods (basically oak) and mixed softwoods (mostly pine) yield about 272 metric tons/day (300 tons/day) and 181 metric tons/day (200 tons/day), respectively. The bleaching sequence on each of the two lines is CHHD.

hardwood pulp to softwood pulp, with the grade change occurring at intervals of approximately 20 to 36 hours. Mill 11 is located in the northern midwest.

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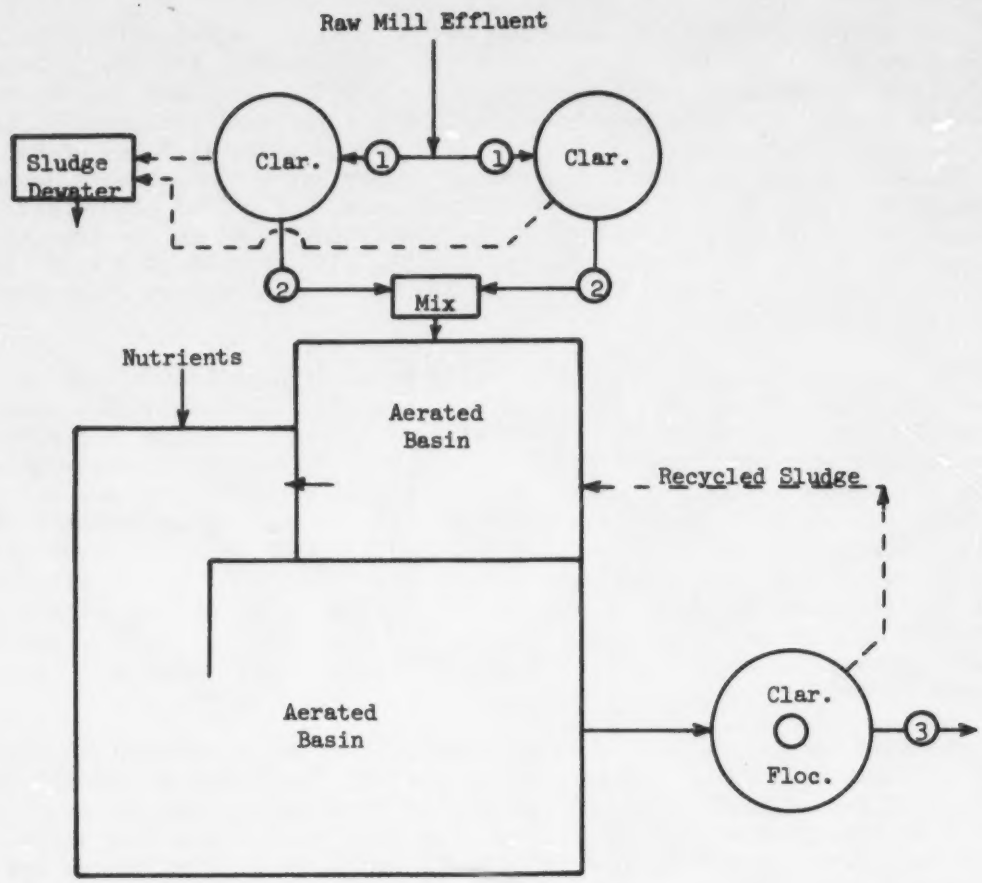


Sampling Points

(1) Raw Effluent (Composite)

(2) Primary Effluent (Composite)

(3) Final Effluent

Figure 13. Mill No. 11 waste treatment system.

TABLE 17. MILL NO. 11 DATA

Mill No. 11; Location: Midwest; Process: bleached kraft and bleached groundwood; Bleach Sequence: CEDED

Wood species: 53-62% hardwood; 38-47% softwood

Waste Treatment System: primary clarifier and lagoon

	Raw			Primary effluent			Final effluent			To condensate steam stripper			From condensate steam stripper		
Sample date	5-3	6-2	7-5	5-3	6-2	7-5	5-3	6-2	7-5	5-3	6-2	7-5	5-3	6-2	7-5
BOD, ppm	330	280	239	292	210	215	43	32	30	8900	10200	7800	2700	3100	1900
Flow rate, m^3/min (gpm)	78.8 (20833)	78.8 (20833)	76.2 (20139)	78.8 (20833)	78.8 (20833)	76.2 (20139)	78.8 (20833)	78.8 (20833)	76.2 (20139)	0.92 (243)	0.92 (243)	0.92 (243)	0.92 (243)	0.92 (243)	0.92 (243)
Production, metric tons/day (short tons/day	590 (651)	613 (676)	668 (736)	590 (651)	613 (676)	668 (736)	590 (651)	613 (676)	668 (736)	590 (651)	613 (676)	668 (736)	590 (651)	613 (676)	668 (736)
pH	6.3	6.4	6.6	6.7	6.9	7.0	7.3	7.2	7.4	--	--	--	--	--	--
Temperature, °C (°F)	40.0 (104)	40.5 (105)	44.4 (112)	38.9 (102)	39.4 (103)	43.3 (110)	21.1 (70)	22.8 (73)	27.2 (81)	--- (--)	-- (--)	-- (--)	-- (--)	-- (--)	-- (--)
Fatty and resin acids, ppm															
Oleic	0.81	0.74	0.38	1.01	0.46	0.33	0.07	<0.02	0.04	0.98	0.75	0.81	0.36	0.08	0.67
Linoleic	3.10	1.86	1.37	2.95	1.03	0.97	0.03	<0.02	0.03	3.17	2.98	2.39	1.81	2.14	2.05
Linolenic	0.05	0.15	0.09	0.07	0.04	0.06	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pimaric	0.19	0.71	0.12	0.13	0.57	N.D.*	0.02	<0.02	<0.02	2.01	3.58*	4.00*	0.76*	2.62*	2.89*
Isopimaric	0.44	0.40	0.26	0.49	0.22	0.15	<0.02	<0.02	0.02	N.D.*	N.D.*	N.D.*	N.D.*	N.D.*	N.D.*
Abietic	1.04	1.20	0.72	0.78	0.59	0.60	<0.02	0.04	0.03	0.26	0.21	0.18	0.08	0.19	0.12
Dehydroabietic	3.33	1.89	1.51	2.34	1.15	1.44	0.15	0.03	0.06	1.11	1.52	1.88	0.46	1.55	1.66
Total	8.96	6.95	4.45	7.77	4.06	3.55	0.27	0.07	0.18	7.53	9.04	9.26	3.47	7.18	7.39
Daily loading															
kg/day	1018	790	489	883	461	390	31	8.2	20	9.98	12.0	12.3	4.58	9.52	9.80
(lb/day)	(2244)	(1741)	(1078)	(1946)	(1017)	(860)	(68)	(18)	(44)	(22.0)	(26.4)	(27.1)	(10.1)	(21.0)	(21.6)
kg/ton	1.82	1.29	0.73	1.50	0.75	0.58	0.05	0.015	0.03	0.017	0.020	0.018	0.008	0.016	0.015
(lb/ton)	(3.45)	(2.58)	(1.46)	(2.99)	(1.50)	(1.17)	(0.10)	(0.03)	(0.06)	(0.034)	(0.039)	(0.037)	(0.017)	(0.031)	(0.029)

(Continued)

*Isopimaric acid was not reported due to a peak in the same area that made computation impossible.

TABLE 17. (Continued)

Sample date	Raw			Primary effluent			Final effluent			To condensate steam stripper			From condensate steam stripper		
	5-3	6-2	7-5	5-3	6-2	7-5	5-3	6-2	7-5	5-3	6-2	7-5	5-3	6-2	7-5
Bleach plant products, ppm															
Trichloroguaiacol	0.100	0.072	0.116	0.215	0.108	0.056	0.072	<0.040	<0.040	--	--	--	--	--	--
Tetrachloroguaiacol	0.060	0.044	0.060	0.096	0.088	<0.040	0.040	<0.040	<0.040	--	--	--	--	--	--
Epoxystearic acid	<0.040	0.452	0.644	<0.040	0.328	0.560	<0.040	<0.040	<0.040	--	--	--	--	--	--
Dichlorostearic acid	0.284	0.256	0.384	0.348	0.188	0.260	0.064	<0.040	<0.040	--	--	--	--	--	--
Monochloro-dehydroabietic acid	0.124	<0.040	0.168	0.100	<0.040	0.124	<0.040	<0.040	<0.040	--	--	--	--	--	--
Dichloro-dehydroabietic acid	0.060	0.120	0.260	0.076	0.072	0.184	<0.040	<0.040	<0.040	--	--	--	--	--	--
Total	0.63	0.94	1.63	0.84	0.78	1.18	0.18	--	--	--	--	--	--	--	--
Daily loading															
kg/day	71.6	107	179	95.4	88.6	130	20.4	--	--	--	--	--	--	--	--
(lb/day)	(157.8)	(235.5)	(394.7)	(210.4)	(195.4)	(285.7)	(45.1)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)
kg/ton	0.12	0.17	0.27	0.16	0.14	0.20	0.03	--	--	--	--	--	--	--	--
(lb/ton)	(0.24)	(0.35)	(0.53)	(0.32)	(0.29)	(0.39)	(0.07)	(--)	(--)	(--)	(--)	(--)	(--)	(--)	(--)
Chloroform, ppm	0.273	0.590	0.413	0.247	0.638	0.521	0.012	Broken	0.008	--	--	--	--	--	--
Daily loading															
kg/day	31.0	67.1	45.4	28.1	72.6	57.2	1.36	--	0.86	--	--	--	--	--	--
(lb/day)	(68.4)	(148)	100)	(61.9)	(160)	(126)	(3.00)	(--)	(1.9)	(--)	(--)	(--)	(--)	(--)	(--)
kg/ton	0.053	0.110	0.068	0.048	0.118	0.086	0.0023	--	0.0013	--	--	--	--	--	--
(lb/ton)	(0.105)	(0.219)	(0.136)	(0.095)	(0.236)	(0.171)	(0.0046)	(--)	(0.0025)	(--)	(--)	(--)	(--)	(--)	(--)

Principal features of the mill's waste treatment facilities, shown in Fig. 14, include primary clarification and a contact-stabilization activated sludge system. Three primary clarifiers [two 22.8 m (75 ft) in diameter and the other 32.3 m (106 ft) in diameter] provide 3.2 to 2.7 hours retention time for 45,000 m^3/day (12 $\overline{M}$ gpd) to 53,000 m^3/day (14 $\overline{M}$ gpd) mill effluent flow. Clarifier overflow rates range from 27.9 m^3/m^2-day (684 gal/day-ft^2) to 32.3 m^3/m^2-day (792 gal/day-ft^2).

The secondary treatment plant consists of three aeration basins in series. One basin is a stabilization tank for reaeration of return sludge, while the other two are contact aerators for aeration of the mixed liquor. For the 45,000 m^3/day (12 $\overline{M}$ gpd) to 53,000 m^3/day (14 $\overline{M}$ gpd) average mill effluent flows and a 40-55% recycle of activated sludge, the stabilization tank provides 3.7 to 2.3 hours retention for return sludge aeration, and the two aeration basins allow for 3.8 to 2.9 hours mixed liquor aeration. Operating characteristics of the plant include a mixed liquor suspended solids of 2500 ppm, a food/microorganism ratio of 0.3-0.35 day^{-1}, and a sludge volume index of 275 ml/g. Four secondary clarifiers in parallel have overflow rates of 24.9 m^3/m^2-day (612 gal/day-ft^2) to 32.3 m^3/m^2-day (792 gal/day-ft^2) and detention times of 3.3-2.5 hours.

Samples taken at the points shown in Fig. 14 included mill raw waste, primary effluent, and secondary effluent. In addition, samples of sludge lagoon supernatant containing primary sludge thickener overflow were also taken. Flow-proportional samples were used on raw mill waste and secondary effluent. Time-intervaled composite samples were taken from the primary effluent, and grab samples of sludge lagoon supernatant were taken at 2-hour intervals. Duration of a sampling period was 8 hours.

Analytical data for samples from Mill 12 are given in Table 18. Daily loadings for bleached toxicants and chloroform are based on bleached pulp production.

MILL 13

Mill 13 is located on the west coast. It produces about 163 metric tons/day (180 tons/day) of pulp from a mixture of pine, Douglas-fir, white fir, and cedar. The bleaching sequence is CEHHD. Paper production is about 363 metric tons/day (400 tons/day).

As shown in Fig. 15, the mill's waste treatment system consists of primary clarification followed by biological treatment in lagoons. Prior to clarification, mill wastes enter either the North Holding Basin (NHB), with a capacity of 7570 m^3 (2.0 $\overline{M}$ gal), the Primary Control Basin (PCB), with a capacity of 2950 m^3 (0.78 $\overline{M}$ gal), or the South Holding Basin (SHB), with a capacity of 7570 m^3 (2.0 $\overline{M}$ gal). Primary clarifier No. 1 treats paper mill waste, for the most part. It has a diameter of 25 m (82 ft), theoretical detention time of 2.6 hours, and rise rate of 29.9 m^3/m^2-day (734 gal/day-ft^2). Primary clarifier No. 2 receives most of the pulp mill effluent. Its diameter is 42.7 m (140 ft), detention time 4.5 hours, and rise rate 23.7 m^3/m^2-day (582 gal/day-ft^2).

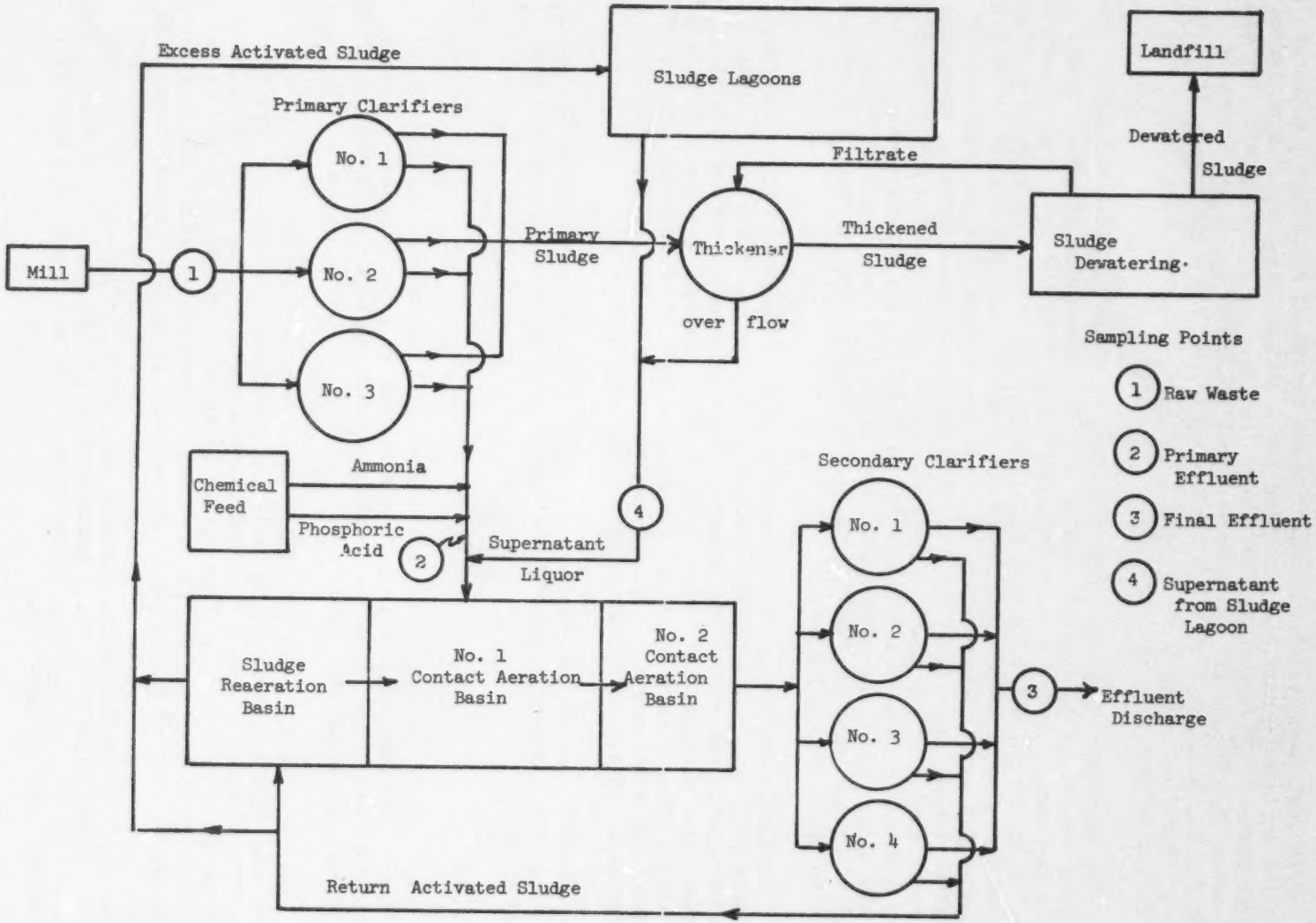


Figure 14. Mill No. 12 waste treatment system.

TABLE 18. MILL NO. 12 DATA

Mill No. 12; Location: East; Process: bleached kraft; Bleach Sequence: CHHD

Wood Species: 61-62% hardwood (oak); 38-39% softwood (pine)

Waste Treatment System: primary clarifier and activated sludge

	Raw			Primary effluent			Final effluent			Sludge lagoon supernatant		
Sampling date	5-4	5-18	6-9	5-4	5-18	6-9	5-4	5-18	6-9	5-4	5-18	6-9
BOD, ppm	324	277	435	249	213	311	7	6	10	137	104	76
Flow rate, m^3/min (gpm)	31.0 (8194)	36.5 (9653)	35.5 (9375)	28.4 (7500)	33.9 (8958)	32.8 (8680)	31.0 (8194)	36.5 (9653)	35.5 (9375)	3.4 (903)	3.4 (903)	3.4 (903)
Production, metric tons/day (short tons/day)	454 (500)	453 (499)	453 (499)	454 (500)	453 (499)	453 (499)	454 (500)	453 (499)	453 (499)	454 (500)	453 (499)	453 (499)
pH	7.2	6.7	6.8	7.1	6.9	7.5	7.8	7.7	7.8	7.6	7.5	7.7
Temperature, °C (°F)	41.7 (107)	41.1 (106)	40.6 (105)	-- (--)	-- (--)	-- (--)	32.8 (91)	35.6 (96)	33.3 (92)	-- (--)	-- (--)	-- (--)
Fatty and resin acids, ppm												
Oleic	0.22	0.08	0.08	0.03	<0.02	0.02	<0.02	<0.02	<0.02	0.03	0.05	0.14
Linoleic	0.18	<0.02	0.25	<0.02	<0.02	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Linolenic	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pimaric	0.09	0.05	0.03	0.04	0.02	<0.02	<0.02	<0.02	<0.02	0.06	<0.02	<0.02
Isopimaric	0.16	0.07	0.10	0.08	<0.02	0.04	<0.02	<0.02	<0.02	0.08	0.03	0.03
Abietic	0.20	0.04	0.02	0.16	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Dehydroabietic	0.35	0.16	0.11	0.32	0.04	0.03	<0.02	<0.02	<0.02	0.04	<0.02	<0.02
Total	1.20	0.40	0.59	0.63	0.06	0.11	--	--	--	0.21	0.08	0.17
Daily loading												
kg/day (lb/day)	53.5 (118)	20.9 (46)	29.9 (66)	25.8 (57)	2.7 (6)	5.0 (11)	-- (--)	-- (--)	-- (--)	1.0 (2.3)	0.4 (0.9)	0.83 (1.84)
kg/ton (lb/ton)	0.12 (0.24)	0.046 (0.092)	0.066 (0.133)	0.057 (0.11)	0.006 (0.012)	0.011 (0.023)	-- (--)	-- (--)	-- (--)	0.0023 (0.0046)	0.0009 (0.002)	0.0018 (0.0037)

(Continued)

TABLE 18. (Continued)

Sampling date	Raw			Primary effluent			Final effluent			Sludge lagoon supernatant		
	5-4	5-18	6-9	5-4	5-18	6-9	5-4	5-18	6-9	5-4	5-18	6-9
Bleach plant products, ppm												
Trichloroguaiacol	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Tetrachloroguaiacol	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Epoxystearic acid	<0.040	<0.040	<0.040	<0.040	<0.040	0.284	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichlorostearic acid	0.176	0.284	0.932	0.252	0.140	0.552	<0.040	<0.040	<0.040	0.176	0.120	<0.040
Monochloro-dehydroabietic acid	0.044	<0.040	0.160	0.084	<0.040	0.116	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichloro-dehydroabietic acid	0.052	0.068	0.148	<0.040	0.072	0.112	<0.040	<0.040	<0.040	<0.040	0.076	<0.040
Total	0.27	0.35	1.24	0.34	0.21	1.1	--	--	--	0.18	0.20	--
Daily loading												
kg/day	12.1	18.4	63.5	13.9	10.2	52.2	--	--	--	0.88	0.98	--
(lb/day)	(26.6)	(40.6)	(140)	(30.7)	(22.6)	(115)	(--)	(--)	(--)	(1.95)	(2.17)	(--)
kg/ton	0.027	0.041	0.14	0.031	0.022	0.12	--	--	--	0.0019	0.0022	--
(lb/ton)	(0.053)	(0.081)	(0.28)	(0.061)	(0.045)	(0.23)	(--)	(--)	(--)	(0.0039)	(0.0044)	(--)
Chloroform, ppm	1.373	1.523	2.258	Broken	1.679	1.805	0.065	0.077	0.083	0.183	0.134	0.140
Daily loading												
kg/day	61.4	80.2	115.4	--	82.0	85.4	2.90	4.06	4.24	0.90	0.66	0.69
(lb/day)	(135.3)	(176.8)	(254.5)	(--)	(180.8)	(188.4)	(6.40)	(8.94)	(9.36)	(1.99)	(1.45)	(1.52)
kg/ton	0.14	0.18	0.26	--	0.18	0.19	0.006	0.009	0.009	0.002	0.001	0.002
(lb/ton)	(0.27)	(0.35)	(0.51)	(--)	(0.36)	(0.38)	(0.013)	(0.018)	(0.019)	(0.004)	(0.003)	(0.003)

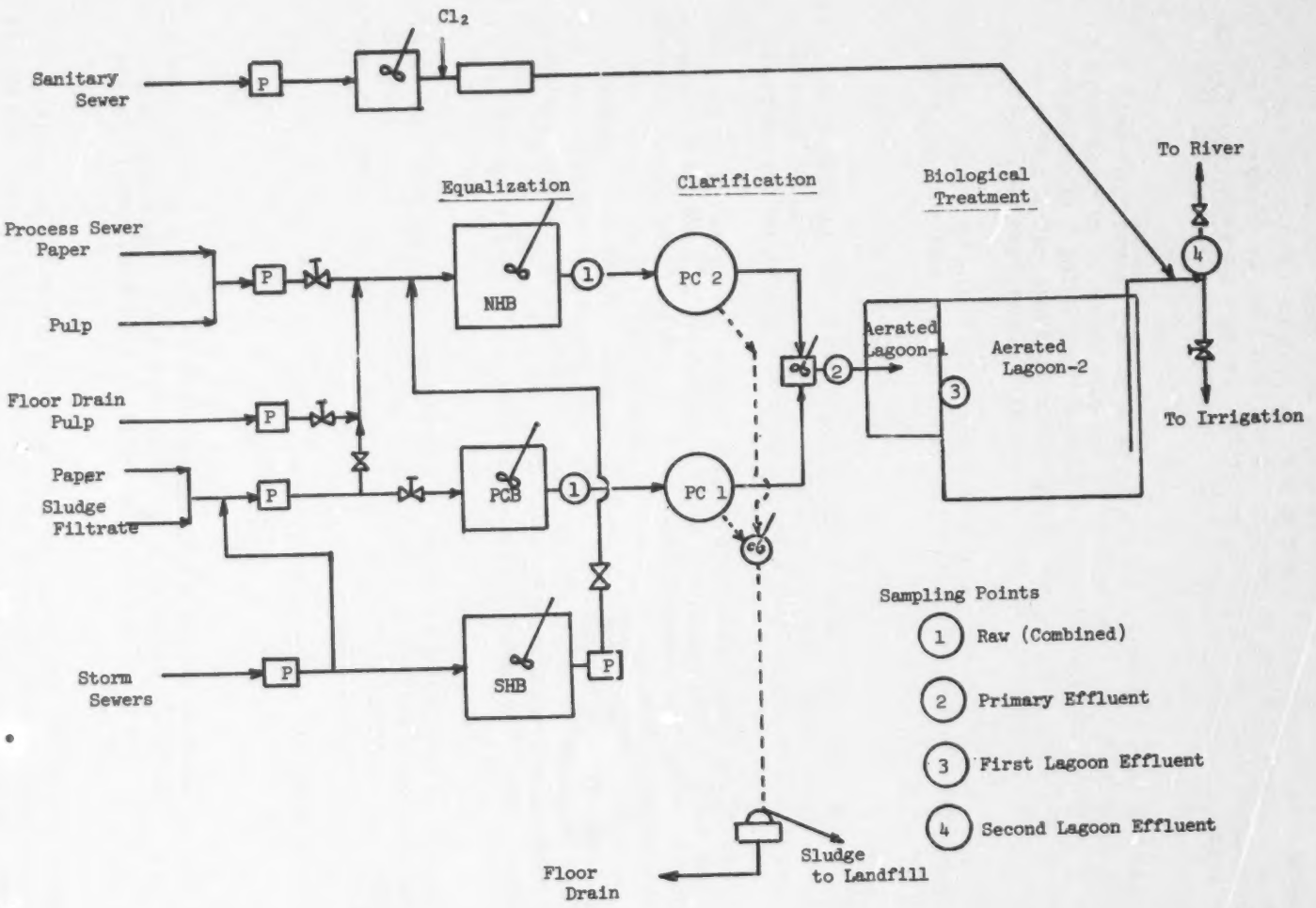


Figure 15. Mill No. 13 waste treatment system.

The first lagoon's area is 1.64 ha (4.1 acres), its depth is 3.36 m (11.0 ft), and its theoretical detention time is 1 day. It has six 56-kw (75-hp) aerators. The second lagoon's area is 10.9 ha (27 acres), its depth is 3.20 m (10.5 ft), and its theoretical detention time is 6 days. This lagoon is divided into two sections, one-third devoted to aeration and two-thirds to settling. The aeration section contains nine 22.4-kw (30-hp) aerators.

Samples for this investigation were taken at the points indicated in Fig. 15. Points 1, 2, and 3 were sampled by hand every 30 minutes for a period of 12 hours. Amounts of sample taken at each Point 1 were weighted in proportion to flow. Point 4 was sampled for 24 hours using a flow proportional automatic sampler. All samples received immediate refrigeration.

Analytical data for these samples are given in Table 19. Daily loadings for bleached toxicants and chloroform are based on bleached pulp production.

MILL 14

Mill 14 is a kraft mill without bleaching located on the west coast. It produces about 1088 metric tons/day (1200 tons/day) of unbleached linerboard from a pulpwood mix of about 80-85% Douglas-fir and 15-20% ponderosa pine.

Waste water treatment facilities, shown in Fig. 16, consist of primary clarification and a completely mixed aerated lagoon. Effluent from the pulp mill, including water from causticizing, cooking, washing, recovery, screening, and hydraulic barker, is fed into a 39.6 m (130 ft) diameter primary clarifier at a rate of about 12.5 m^3/min (3300 gpm). Paper mill effluent, after clarification in a dissolved air flotation system, is added to the pulp mill effluent at about 9.5 m^3/min (2500 gpm). Combined effluents receive final treatment in a lagoon with an area of 8.5 ha (21 acres) and 4.5-5.5 days detention time. The lagoon contains 11 aerators with a total of 615 kw (825 hp).

Samples for this study were taken at the points shown in Fig. 16. Except for the secondary effluent, samples were composites of 4 grabs taken at 2-hour intervals. Secondary effluent was sampled automatically over 24 hours to yield a time-intervaled composite.

Analytical data are shown in Table 20.

MILL 15

This mill is located in the south and produces about 454 metric tons/day (500 tons/day) of bleached kraft pulp and about 544 metric tons/day (600 tons/day) of coated board. The bleaching sequence is CEDED. Wood species used are pine, oak, and gum.

For waste treatment, this mill uses a primary clarifier, an aerated lagoon, and polishing ponds, as shown in Fig. 17. In this project the mill's final effluent was also subjected to a tertiary treatment, a bench-scale alum precipitation.

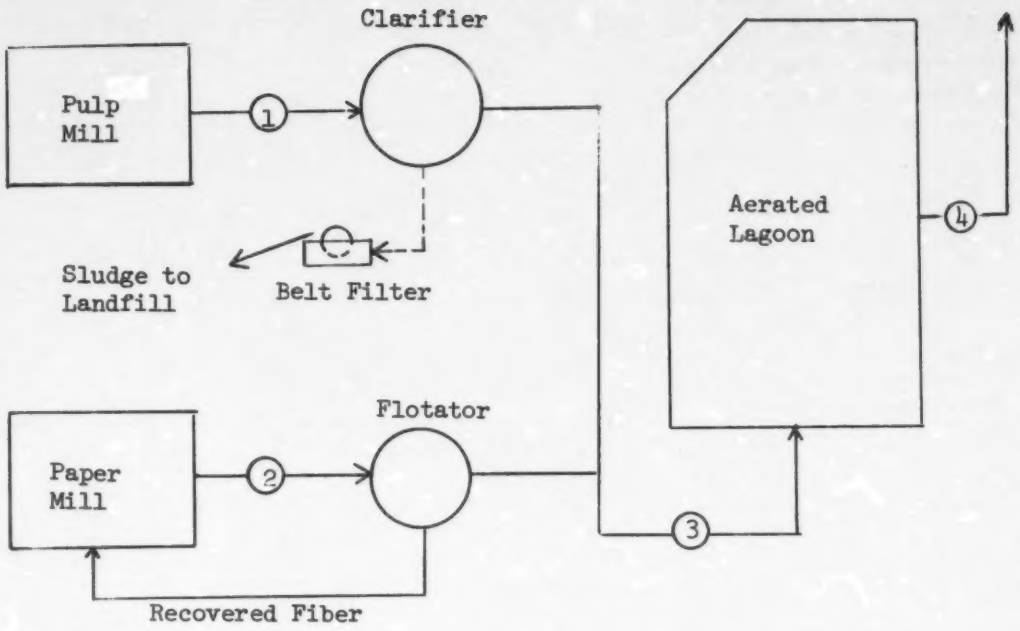
TABLE 19. MILL NO. 13 DATA

Mill No. 13; Location: West Coast; Process: bleached kraft; Bleach Sequence: CEHHD

Wood Species: 30-35% pine; 30-35% Douglas-fir; 20-25% white pine; 10-15% cedar

Waste Treatment System: primary clarifier and aerated lagoon

	Raw combined		Primary		1st Lagoon		2nd Lagoon	
Sampling date	4-18	5-16	4-18	5-16	4-18	5-16	4-18	5-16
BOD, ppm	159	264	179	183	37	60	7.7	12.5
Flow rate, m^3/min (gpm)	30.3 (8000)	30.3 (8000)	30.3 (8000)	30.3 (8000)	30.3 (8000)	30.3 (8000)	33.4 (8830)	28.9 (7625)
Production, metric tons/day (short tons/day)	165 (182)	163 (180)	165 (182)	163 (180)	165 (182)	163 (180)	165 (182)	163 (180)
pH	9.4	10.9	8.5	11.0	8.0	9.2	6.8	7.0
Temperature, °C (°F)	33.9 (93)	32.4 (90)	33.9 (93)	34.8 (95)	27.7 (82)	31.6 (89)	23.5 (74)	24.5 (76)
Fatty and resin acids, ppm								
Oleic	0.29	0.38	0.11	0.33	<0.02	<0.02	<0.02	<0.02
Linoleic	0.14	0.12	0.03	0.12	<0.02	<0.02	<0.02	<0.02
Linolenic	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pimaric	0.08	0.10	0.08	0.12	0.02	0.09	<0.02	<0.02
Isopimaric	0.33	0.37	0.39	0.50	0.14	0.26	<0.02	<0.02
Abietic	0.36	0.18	0.37	0.24	0.07	<0.02	<0.02	<0.02
Dehydroabietic	0.55	0.34	0.38	0.54	0.07	<0.02		
Total	1.75	1.49	1.36	1.85	0.30	0.35	--	--
Daily loading kg/day (lb/day)	76.2 (168)	65 (143)	59 (130)	80.7 (178)	13.2 (29)	15.3 (34)	-- (--)	-- (--)
kg/ton (lb/ton)	0.46 (0.92)	0.40 (0.79)	0.36 (0.71)	0.50 (0.99)	0.08 (0.16)	0.09 (0.19)	-- (--)	-- (--)
Bleach plant products, ppm								
Trichloroguaiacol	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Tetrachloroguaiacol	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Epoxystearic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichlorostearic acid	0.248	0.160	0.208	0.108	<0.040	<0.040	<0.040	<0.040
Monochloro-dehydroabietic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichlorodehydro-abietic acid	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Total	0.25	0.16	0.21	0.11	--	--	--	--
Daily loading kg/day (lb/day)	11 (24)	7.0 (15.4)	9.1 (20)	4.8 (10.6)	(--)	(--)	(--)	(--)
kg/ton (lb/ton)	0.06 (0.13)	0.04 (0.08)	0.05 (0.11)	0.03 (0.06)	-- (--)	-- (--)	-- (--)	-- (--)
Chloroform, ppm	0.325	0.518	0.401	0.514	0.068	0.085	0.009	0.008
kg/day (lb/day)	14.2 (31.3)	22.6 (50)	17.5 (38.6)	22.4 (49)	3.0 (6.5)	3.7 (8.2)	0.43 (0.95)	0.33 (0.73)
kg/ton (lb/ton)	0.08 (0.17)	0.14 (0.28)	0.10 (0.21)	0.14 (0.27)	0.02 (0.04)	0.02 (0.04)	0.003 (0.005)	0.002 (0.004)



Sampling Points

1. Pulp Mill Effluent
2. Paper Mill Effluent
3. Primary Effluent
4. Final Effluent

Figure 16. Mill No. 14 waste treatment system.

TABLE 20. MILL NO. 14 DATA

Mill No. 14; Location: Northwest; Process: unbleached kraft

Wood Species: 80-85% Douglas-fir, 15-20% pine

Waste Treatment: primary clarifier and lagoon

	Pulp mill effluent			Paper mill effluent			Primary			Secondary		
Sampling date	5-19	5-26	6-16	5-19	5-26	6-16	5-19	5-26	6-16	5-19	5-26	6-16
BOD, ppm	635	28[illegible]	705	370	312	450	390	272	395	36	28	28
Flow rate, m^3/min (gpm)	12.7 (3350)	12.2 (3230)	12.5 (3310)	9.10 (2400)	7.9 (2100)	9.5 (2500)	25.1 (6630)	25.8 (6825)	26.6 (7035)	25.1 (6630)	25.8 (6825)	26.6 (7035)
Production, metric tons/day (short tons/day)	997 (1099)	883 (973)	1037 (1143)	997 (1099)	883 (973)	1037 (1143)	997 (1099)	883 (973)	1037 (1143)	997 (1099)	883 (973)	1037 (1143)
pH	10.2	10.8	9.8	6.9	6.3	6.0	10.1	10.4	10.0	7.3	7.6	7.3
Temperature, °C (°F)	-- (--)	-- (--)	-- (--)	-- (--)	-- (--)	-- (--)	46.1 (115)	43.9 (111)	50.0 (122)	27.8 (82)	28.3 (83)	30.0 (86)
Fatty and resin acids, ppm												
Oleic	1.57	0.10	0.18	0.33	0.05	0.41	0.53	0.11	0.23	<0.02	0.12	0.04
Linoleic	1.12	<0.02	0.18	0.10	0.06	0.49	0.44	<0.02	0.05	<0.02	<0.02	<0.02
Linolenic	0.11	<0.02	0.03	<0.02	<0.02	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pimaric	0.10	0.17	0.28	0.16	<0.02	0.28	0.17	0.22	0.25	<0.02	0.04	0.02
Isopimaric	4.12	2.49	3.60	0.91	0.21	0.95	1.77	2.37	2.10	<0.02	0.02	0.02
Abietic	1.34	1.31	1.03	0.61	0.23	1.04	0.88	1.08	0.86	<0.02	<0.02	0.03
Dehydroabietic	1.58	1.20	1.49	1.91	0.55	1.75	1.51	1.21	1.52	<0.02	<0.02	0.06
Total	9.94	5.27	6.79	4.02	1.10	4.94	5.30	4.99	5.01	--	0.18	0.17
Daily loading												
kg/day	181	93.0	122	53.1	12.6	67.1	192	186	191	--	6.7	6.5
(lb/day)	(400.0)	(205)	(270)	(117)	(27.7)	(148)	(423)	(410)	(422)	(--)	(14.8)	(14.3)
kg/ton pulp	0.18	0.10	0.12	0.05	0.01	0.06	0.19	0.21	0.18	--	0.007	0.006
(lb/ton pulp)	(0.36)	(0.21)	(0.24)	(0.11)	(0.03)	(0.13)	(0.38)	(0.42)	(0.37)	(--)	(0.015)	(0.012)

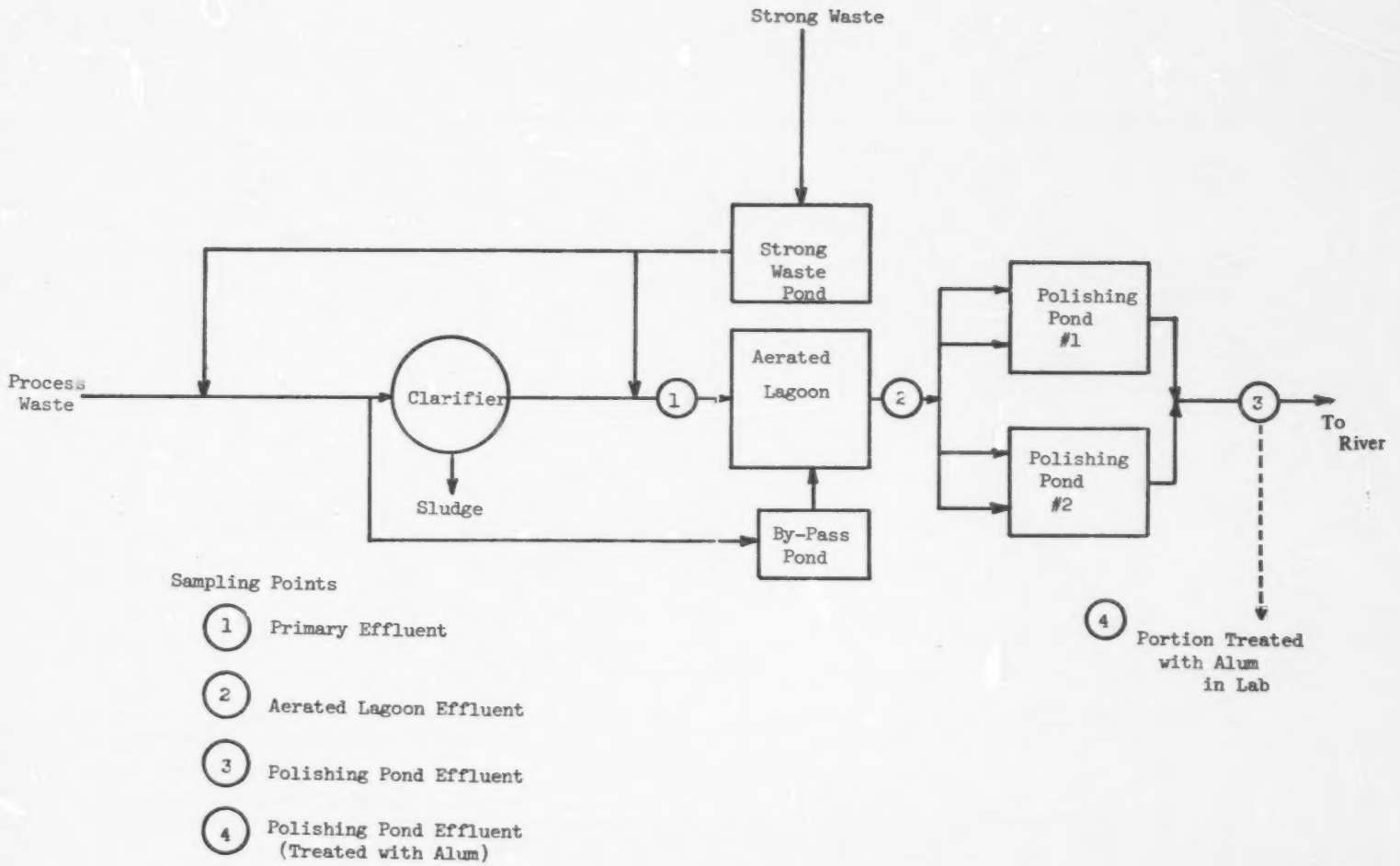


Figure 17. Mill No. 15 waste treatment system.

Strong waste, indicated in Fig. 17, consists of waste occurring around the digester, and from washing and screening. Process waste comes from the board machine, the bleach plant, and from treatment of fresh intake water from the river. These wastes pass into the primary clarifier, which has a diameter of 83.8 m (275 ft). Effluent from the clarifier enters the aerated lagoon, which has an area of 19.8 ha (49 acres), a depth of 4.6 m (15 ft), a capacity of 999,000 m^3 (264 M gal), and a detention time of 15 days. Aeration is achieved by three blowers driven by 298-kw (400-hp) motors which convey 696 m^3 (24,600 ft^3) of air per minute to 1120 static aerators in the lagoon. From the aerated lagoon, effluent flows to a quiescent stabilization lagoon (polishing pond) which has an area of 12.1 ha (30 acres), a depth of 4.6 m (15 ft), a capacity of 450,000 m^3 (119 M gal), and a detention time of 7 days. A second, identical, stabilization lagoon is kept empty for emergency use.

Samples were taken from the mill's waste treatment system at the points indicated in Fig. 17. Hourly grab samples were taken for 24 hours from the clarifier effluent and the aerated lagoon effluent. They were stored as a composite at 4.4°C (40°F). Effluent from the stabilization lagoon was sampled continuously into an iced sample container.

Bench-scale alum precipitations were conducted on 1-liter samples of effluent from the stabilization lagoon. About 4.5 cm^3 (1 tsp) of alum sludge ash were added, and pH was adjusted to pH 4.5-5.0 with water plant alum. Four drops of anionic polymer were added and the sample was allowed to settle.

Analytical data are given in Table 21. Daily loadings for bleached toxicants and chloroform are based on bleached pulp production.

TABLE 21. MILL NO. 15 DATA

Mill No. 15; Location: South; Process: bleached kraft; Bleach Sequence: CEDED

Wood Species: 35% pine; 65% hardwood (60% oak, rest gum)

Waste Treatment System: primary clarifier, aerated lagoon and stabilization lagoon

Sampling date	Primary clarifier			Aerated basin effluent			Polishing pond			Polishing pond, treated		
	6-1	6-8	6-15	6-1	6-8	6-15	6-1	6-8	6-15	6-1	6-8	6-15
BOD, ppm	256	465	315	56	59	99	43	42	51	14	0	5
Flow rate, m^3/min (gpm)	49.7 (13125)	50.7 (13403)	48.6 (12847)	49.7 (13125)	50.7 (13403)	48.6 (12847)	49.7 (13125)	50.7 (13403)	48.6 (12847)	-- (--)	-- (--)	-- (--)
Production, metric tons/day (short tons/day)	444 (489)	467 (515)	347 (383)	444 (489)	467 (515)	347 (383)	444 (489)	467 (515)	347 (383)	444 (489)	467 (515)	347 (383)
pH	8.2	9.3	7.3	8.3	8.0	7.4	8.3	7.8	7.7	5.0	4.4	4.5
Temperature, °C (°F)	-- (--)	-- (--)	-- (--)	-- (--)	-- (--)	-- (--)	-- (--)	-- (--)	-- (--)	-- (--)	-- (--)	-- (--)
Fatty and resin acids, ppm												
Oleic	2.22	7.75	6.71	0.48	0.36	1.47	0.54	0.28	0.32	<0.02	<0.02	<0.02
Linoleic	1.39	4.85	4.27	0.03	0.05	0.46	0.03	0.03	0.04	<0.02	<0.02	<0.02
Linolenic	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pimaric	0.44	1.01	0.91	0.42	0.33	0.38	0.54	0.37	0.32	<0.02	<0.02	<0.02
Isopimaric	0.35	0.76	0.85	0.45	0.30	0.40	0.45	0.37	0.24	<0.02	<0.02	<0.02
Abietic	1.36	3.59	3.89	0.66	0.85	1.65	1.14	0.92	0.95	<0.02	<0.02	<0.02
Dehydroabietic	2.17	3.75	3.12	0.66	0.69	1.43	1.05	0.86	0.95	<0.02	<0.02	<0.02
Total	7.93	21.71	19.75	2.70	2.58	5.79	3.75	2.83	2.82	--	--	--
Daily loading												
kg/day (lb/day)	567 (1251)	1587 (3499)	1384 (3051)	193 (426)	189 (416)	405 (894)	268 (592)	207 (456)	198 (436)	-- (--)	-- (--)	-- (--)
kg/ton (lb/ton)	1.28 (2.56)	3.40 (6.79)	3.99 (7.96)	0.43 (0.87)	0.40 (0.81)	1.17 (2.33)	0.60 (1.21)	0.44 (0.88)	0.57 (1.14)	-- (--)	-- (--)	-- (--)

(Continued)

TABLE 21. (Continued)

Sampling date	Primary clarifier			Aerated basin effluent			Polishing pond			Polishing pond, treated		
	6-1	6-8	6-15	6-1	6-8	6-15	6-1	6-8	6-15	6-1	6-8	6-15
Bleach plant products, ppm												
Trichloroguaiacol	0.052	<0.040	0.064	0.124	0.080	0.092	0.048	0.044	0.052	<0.040	<0.040	<0.040
Tetrachloroguaiacol	0.040	<0.040	0.064	0.088	0.060	0.076	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Epoxystearic acid	0.116	1.54	1.12	<0.040	0.044	0.316	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichlorostearic acid	0.416	0.532	0.372	0.296	0.316	0.264	0.268	0.252	0.248	<0.040	0.040	<0.040
Monochloro-dehydroabietic acid	0.068	<0.040	<0.040	0.040	0.044	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040	<0.040
Dichloro-dehydroabietic acid	0.124	0.136	0.180	0.300	0.276	0.236	0.112	0.152	0.132	<0.040	<0.040	<0.040
Total	0.82	2.2	1.8	0.85	0.82	0.98	0.43	0.45	0.43	--	0.040	--
Daily loading												
kg/day	58.7	161	126	60.8	59.9	68.7	30.8	32.9	30.1	--	2.9	--
(lb/day)	(129)	(354)	(278)	(134)	(132)	(151)	(67.9)	(72.5)	(66.4)	(--)	(6.4)	(--)
kg/ton	0.13	0.34	0.36	0.14	0.13	0.20	0.07	0.07	0.09	--	0.006	--
(lb/ton)	(0.26)	(0.69)	(0.73)	(0.27)	(0.26)	(0.40)	(0.14)	(0.14)	(0.17)	(--)	(0.012)	(--)
Chloroform, ppm	1.070	0.857	0.984	0.063	0.061	0.269	0.032	0.022	0.025	0.018	0.020	0.022
Daily loading												
kg/day	76.6	62.6	68.9	4.51	4.46	18.9	2.29	1.60	1.75	1.29	1.46	1.54
(lb/day)	(168.9)	(138.1)	(152.0)	(9.94)	(9.83)	(41.6)	(5.05)	(3.54)	(3.86)	(2.84)	(3.22)	(3.40)
kg/ton	0.17	0.13	0.20	0.01	0.01	0.05	0.005	0.003	0.005	0.003	0.003	0.004
(lb/ton)	(0.34)	(0.27)	(0.40)	(0.02)	(0.02)	(0.11)	(0.01)	(0.007)	(0.01)	(0.006)	(0.006)	(0.009)

SECTION 8

DISCUSSION OF RESULTS*

GENERAL OBSERVATIONS

Data showing removal of fatty and resin acids, bleach toxicants (bleach plant products), chloroform, BOD, and suspended solids for each of the mills studied are summarized in Table 22. Immediately evident and of greatest significance is the indication that nearly all of the systems studied removed essentially all of the materials of interest quite effectively. Consequently, the discussions in the following sections of this report will deal with subtle differences between mills and processes rather than the gross ability or inability to remove a specific toxicant. Mills in Table 22 that achieved 90 or more percent removal of each of the parameters studied include Mills 1, 5 (when alum treatment was used), 12, and 13. Mills 8 and 14 dropped below 90% removal only on suspended solids.

Chloroform was removed effectively in nearly all of the mill-scale waste treatment systems. Volatilization is one suspected removal mechanism. Amounts of chloroform in final mill effluents (8-75 ppb) are in the range that has been reported for some municipal drinking waters (2-152 ppb) (14).

Average levels of total fatty and resin acids in mill effluents shown in Table 22 ranged from a few ppb to 9.0 ppm. The detection limit for an individual compound was 20 ppb. Bleach plant toxicant concentrations were lower than the concentrations of fatty and resin acids; the highest average was 0.44 ppm. The detection limit for the bleach plant toxicants was 40 ppb.

The mills' individual data tables indicate that very little removal of fatty and resin acids or bleach toxicants occurred during primary clarification. This suggests that these compounds were not associated with the suspended solids removed during that treatment. Mill 12 was an exception, with significant removal (63%) of fatty and resin acids but not bleach toxicants occurring in the clarifier.

BIOLOGICAL PROCESSES

Sulfite Mills

Raw effluents from the two sulfite mills in the program, Mill 7 and Mill 10, were characterized by their low concentrations of fatty and resin acids.

*Pulping process, location, and waste treatment process of each of the participating mills (listed by code number) are shown in Table 1, p. 5.

TABLE 22. SUMMARY OF WASTE TREATMENT EVALUATION

(All values represent an average of three samplings)

Mill	Treatment	Fatty and resin acids			Bleach toxicants			Chloroform			BOD			Suspended solids		
		Raw, ppm	Final, ppm	Removal,[1] %	Raw, ppm	Final, ppm	Removal, %	Raw, ppm	Final, ppm	Removal, %	Raw, ppm	Final, ppm	Removal, %	Raw, ppm	Final, ppm	Removal, %
1	Reverse osmosis & recycle	25.5	0.1	∿100	——— mill without bleaching ———						10,640	48	∿100	295	19	94
2	Ultrafiltration on caustic extract only	bleach plant only			13.5	8.5	37	1.19	2.31	0	—— not reported ——			77	5.1	93
3	Ultrafiltration on caustic extract only	bleach plant only			13.4	2.4	82	0.126	0.101	20	457	111	76	—— not reported ——		
4	Primary clarifier & oxygen-activated sludge	24.8	8.5	66	1.04	0.43	59	0.43	0.05	88	574	60	90	—— not reported ——		
5[2]	Oxygen-activated sludge & alum treatment	7.9	1.8 (none)	77 (∿100)	——— mill without bleaching ———						237	34 (7.2)	86 (97)	72	133 (7.5)	-- (90)
6	Lime color removal & recarbonation	30.7	6.9	78	——— mill without bleaching ———						246	168	32	—— not reported ——		
7	Activated sludge no primary	1.75	0.29	83	none	none	--	1.30	0.040	97	1793	67	96	not reported	66	--
8	Primary clarifier & activated sludge	9.3	0.2	98	0.09	none	∿100	1.48	0.06	96	240	14	94	322	58	82
9	Primary clarifier & lagoon	28.7	9.0	69	——— mill without bleaching ———						305	65	79	244	83	66
10	Primary clarifier & lagoon	1.58	0.05	97	trace	none	--	0.091[3]	0.009	90	168[4]	34	80	—— not reported ——		
11	Primary clarifier & lagoon	6.8	0.2	97	1.07	0.06	94	0.425	0.010	98	283	35	88	—— not reported ——		
12	Primary clarifier & activated sludge	0.73	none	∿100	0.62	none	∿100	1.72	0.075	96	345	8	98	515	36	93
13	Primary clarifier & lagoon	1.62	none	∿100	0.20	none	∿100	0.422	0.008	98	212	10	95	856	24	97
14	Primary clarifier & lagoon	5.7	0.1	98	——— mill without bleaching ———						473	33	93	517	67	85
15[5]	Primary clarifier, aerated lagoon, stabilization lagoon	16.5	3.11 (none)	81 (∿100)	1.61	0.44 (0.01)	73 (98)	0.97	0.026 (0.020)	97 (98)	345	45 (6)	87 (98)	84	22 (34)	74 (60)

[1]Percentage removal was calculated by the following equation: Removal, % = 100 (Raw conc. − final conc.)/raw conc. In reverse osmosis and ultrafiltration the permeate was considered the final effluent.

[2]Mill 5 did not submit a raw sample. Calculations are based on the primary effluent. The values in parentheses are for the alum treated secondary effluents.

[3]Bleach plant waste by-passes primary. Input to secondary was used as raw.

[4]No BOD's were reported on raw waste. BOD's reported for input to secondary were used as raw.

[5]Mill 15 did not submit raw samples. The values in the raw column represent the primary effluent. The values in parentheses represent alum bench-treated polishing pond effluents.

These concentrations, which were less than those exhibited by most of the kraft mills, were further reduced in secondary treatment. Mill 10's two-cell lagoon facility achieved a greater removal of these compounds (97%) than did Mill 7's activated sludge plant (83%). The apparent removal of fatty and resin acids in Mill 10's primary clarifier was only a dilution by bleach effluent. Raw effluents from these mills contained little or no bleach toxicants; levels in the final effluents were below the detection limit.

Kraft Mills

Included in this investigation were kraft mills which used oxygen-activated sludge, air-activated sludge (usually called simply activated sludge), and aerated lagoons. Some of the data obtained on these systems are summarized in Table 23 and are plotted in Figs. 18 and 19. Data in both figures suggest a trend toward less complete removal of fatty and resin acids in those systems which received heavier resin and fatty acid loading. Based upon the limited number of mills sampled, the air-activated sludge systems performed as well as or better than the lagoons, while the two oxygen-activated sludge systems achieved somewhat lower percentage removal of fatty and resin acids. As illustrated in Fig. 18, the performance of the oxygen-activated sludge systems might be explained by their receiving a heavier daily loading of fatty and resin acids per kg MLSS than did the air-activated sludge systems. Under the conditions of operation at the time of this study, the oxygen-activated sludge systems demonstrated a higher percentage removal of BOD than of the toxic compounds.

Data in Table 22 show that only three of the kraft mills with biological waste treatment had measurable amounts of the bleach toxicants in their secondary treatment plant effluents (Mills 4, 11, and 15). The relative ability of these mills to remove the bleach toxicants paralleled their relative ability to remove fatty and resin acids. In each case, the percentage removal of the bleach toxicants was less than the percentage removal of the unchlorinated fatty and resin acids. This behavior is consistent with the reported biodegradability of these compounds (7).

PRECIPITATION PROCESSES

Precipitation processes yielded substantial reductions in concentration of the compounds of interest in each of the three mills studied. In Mill 6, lime treatment removed 78% of the fatty and resin acids from waste streams containing an average of over 30 ppm of those compounds. BOD removal, averaging 32%, is typical of what has been reported previously for that installation. Because the lime treatment system was designed for removal of color rather than BOD, its ability to remove these toxic compounds might be considered an unexpected benefit.

When used as a tertiary treatment, as in Mills 5 and 15, alum precipitation reduced fatty and resin acids and bleach toxicants to near or below limits of detection. In these mills, the streams entering the treatment contained rather light loadings of the compounds of interest (in contrast with Mill 6, above). It must be noted, however, that because the mill-scale alum

TABLE 23. LOADING AND REMOVAL OF FATTY AND RESIN ACIDS AND BOD IN BIOLOGICAL TREATMENT SYSTEMS

Mill	System	Fatty and resin acids			BOD		
		kg/day/kg MLSS	kg/day/1000 m^3 [1]	Removal, %	kg/day/kg MLSS	kg/day/1000 m^3 [1]	Removal, %
4	Oxygen-activated sludge	0.045	—	68	0.85	--	88
5	Oxygen-activated sludge	0.025	--	77	∿1	--	89
8	Air-activated sludge	0.0043	--	98	0.12	--	95
9	Lagoon	--	2.4	63	--	28	77
11	Lagoon	--	0.48	97	--	22	85
12	Air-activated sludge	0.00032	--	∿100	0.32	--	97
13	Lagoon	--	0.17	∿100	--	20	94
14	Lagoon	--	0.67	98	--	46	91
15	Lagoon[2]	--	1.2	78	--	25	79

Data in this table refer only to secondary systems treating kraft mill effluent.

[1]Lagoon volume.

[2]Treatment in polishing pond not included.

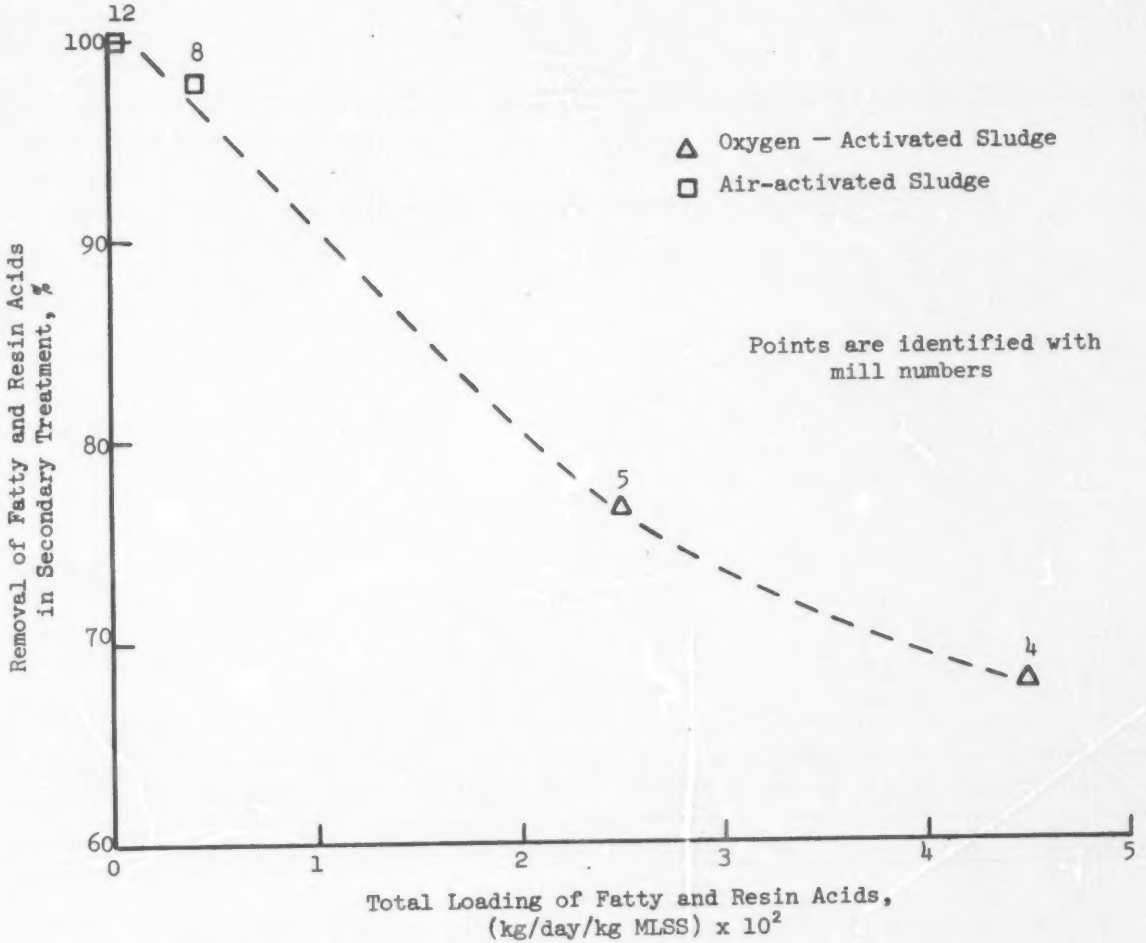


Figure 18. Removal of fatty and resin acids in activated sludge systems.

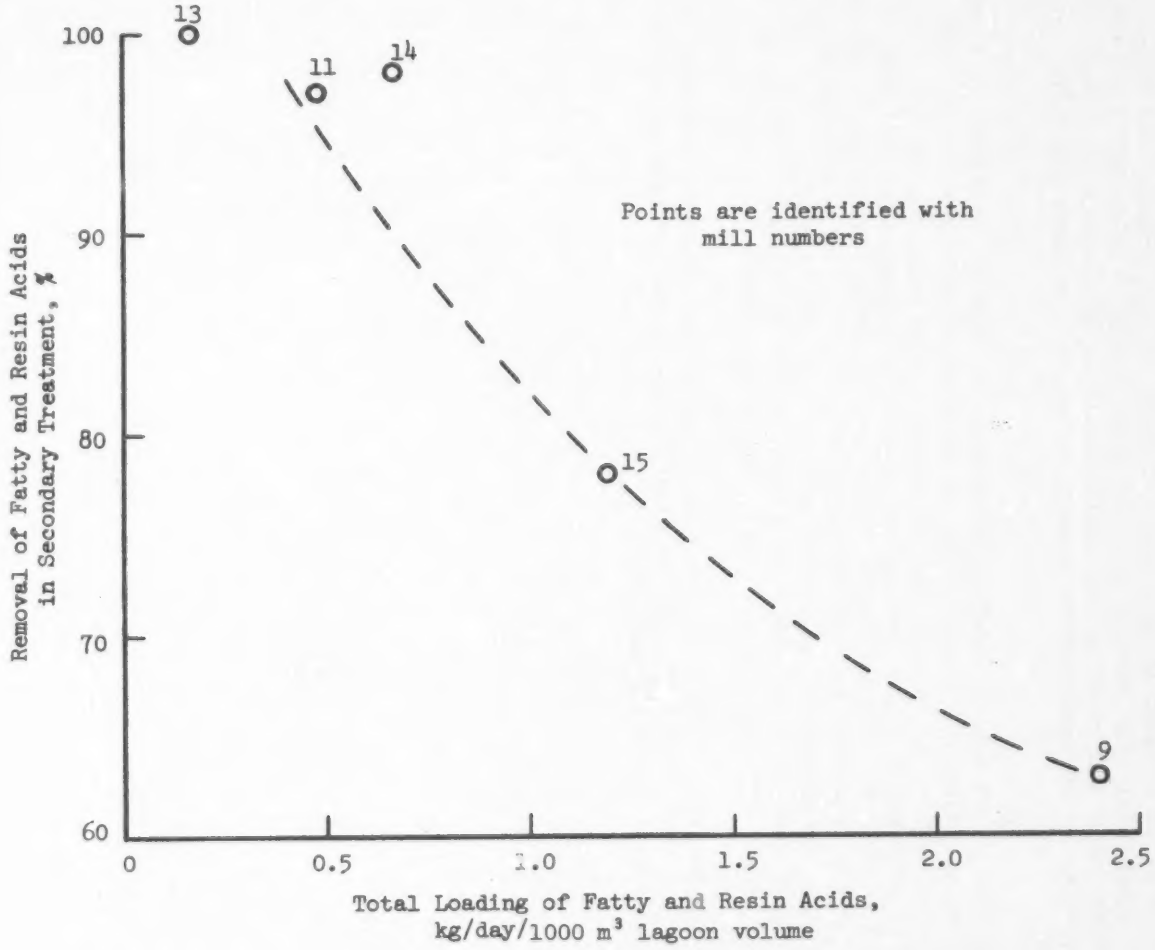


Figure 19. Removal of fatty and resin acids in aerated lagoons.

treatment system at Mill 5 was not operating, the alum precipitations for both Mill 5 and Mill 15 were conducted in the laboratory.

MEMBRANE PROCESSES

Three mills studied in this investigation employ membrane processes. Using a commercial size reverse osmosis system, Mill 1 achieved ~100% removal of BOD and fatty and resin acids. This result is consistent with the recognized ability of RO membranes to retain low as well as high molecular weight solutes.

The two pilot ultrafiltration units (Mills 2 and 3) operated on caustic extraction filtrate. Concentrations of the bleach toxicants in the feed (before prefiltration) to each of the units were quite similar, yet the UF unit in Mill 3 achieved a higher percentage removal of these compounds than was achieved in Mill 2. The membranes on the two UF units were quite dissimilar. Mill 2 used a synthetic polymer membrane, and Mill 3 used a membrane formed from hydrous zirconium and silicon oxides. Apparently the characteristics of the membrane used in Mill 3 were such that it tended to retain compounds whose molecular size was that of the bleach toxicants.

The chloroform content of the caustic extraction filtrate was much higher in Mill 2 than in Mill 3. In both cases, the chloroform passed through the UF membranes virtually unimpeded.

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